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The Development and Optimization of an Ethylbenzene Process

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THE DEVELOPMENT AND OPTIMIZATION OF AN ETHYLBENZENE PROCESS

By
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ABSTRACT

The purpose of this thesis was to optimize a pre-existing vapor phase ethylbenzene process, and to develop a base case liquid phase ethylbenzene process. A brief introduction is included to present an overview of process optimization and suggest common strategies to employ. While optimizing the vapor phase process, discrete optimization was performed to determine the local optima for multiple unit operations by comparing their net present value to that of the base case. After optimization, an $81.5 million increase in net present value was obtained. When developing the liquid phase ethylbenzene process, Antoine's Equation, Raoult's Law, the first law of thermodynamics, and material and energy balances were used to create a base case for a process that produced 80,000 tonnes per year of 99.8 mol% ethylbenzene. This included the creation of a process flow diagram, equipment and utility tables, and stream tables containing temperature, pressure, and component molar flow rates. Explanations as to how the results were obtained and the conclusions of the study are presented.

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LIST OF ABBREVIATIONS

NPV	net present value
EAOC	equivalent annual operating cost
ppm	parts per million
DEB	diethylbenzene
EB	ethylbenzene
PFD	process flow diagram
MARR	minimum accepted rate of return
FCI	fixed capital investment
BFD	block flow diagram
CSTR	continuous-stirred tank reactor
atm	atmosphere

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SECTION I: A Brief Introduction to Process Optimization

For all processes, especially chemical processes, it is important to determine the conditions at which the process runs at its "best." The "best" and how it is defined differs from process to process. However, the general overview for establishing the best conditions remains constant. This is referred to as the optimization of a process. When optimizing a process, a situation or system must already exist, and it is understood that there is room for improvement. In this section, the common terms and procedure followed for the optimization of a chemical process are introduced and explained.

First, per the definition of optimization, a process or system has already been established. The starting point is denoted the "base case" and is the point of reference when determining if a new value is better or worse for the process. To first begin optimization, it is essential to establish what the objective function, or the measure of value, is for the process. Usually, the objective is to maximize the net present value (NPV) or profit or minimize the equivalent annual operating cost (EAOC), and often has units of dollars. However, the objective is specific to the process and could include minimizing the concentration of a contaminant in a stream or maximizing the production of the desired product. Once the objective function and the goal for the process has been established, the design variables and constraints of the process must be identified. The design variables are the independent variables that can be changed such as temperature or the number of stages in a column. The constraints for a process are the limitations to the design variables, such

as a temperature range for efficient catalyst operation. Finally, a global optimum is the point at which the process is found to be its absolute best. Any deviation from these design variables would result in a less desirable value for the objective function. However, determining the global optimum is difficult, extremely time consuming, and highly unlikely due to constantly changing process and economic parameters. For this, the local optimum is usually determined, which is the optimal value determined for each design constraint.

Because chemical processes generally are high in complexity, it is easy to become lost in the small details while optimizing. To counter this, the top-down strategy for optimization has been established. With this strategy, the big picture is examined first, followed by analysis of the smaller details that could prove important. From the big picture, two types of optimizations are often encountered. These include topological optimization and parametric optimization. Topological optimization is the improvement of the topology, or arrangement of the equipment. Examples of optimization for this include elimination of unwanted by-products, elimination or rearrangement of equipment, alternative methods for separation or reaction configurations, and heat integration. When performing topological optimization, these examples should be addressed sequentially. Topological optimization should generally be considered prior to parametric optimization, as it allows for a fixed process and could largely affect the objective function. However, during parametric optimization, it is sometimes necessary to revisit topological optimization due to the change in design variables. Parametric optimization differs from topological in that it is the optimization of key design variables and focuses specifically on unit operations. Important variables to be optimized should be identified early in this process. Common key variables

for chemical processes include the operating conditions for the reactor, single-pass conversion in the reactor, recovery of unused reactants, purity of products, reflux ratio and component recovery in columns, and operating pressure of separators. Depending on the process, some of these will be considered key variables, while some may not. However, it is important to determine this. From there, analysis of each variable should be performed to determine the local optimum. Additionally, while implementing parametric optimization, it is common for the requirements and costs of utilities to change due to the changes in operating conditions. To adequately compare the changes to the base case, it is important to include the corresponding utility changes.

To analyze the aforementioned design variables during parametric optimization, there are multiple suggested strategies. These strategies include the response surface analysis and lattice search techniques. For response surface analysis, somewhat arbitrary ranges for variation of the key design variables are chosen. These are termed somewhat arbitrary in that they can be chosen based on general theory regarding that variable or actual constraints presented by the process, such as maximum operating temperature for a catalyst. From these ranges, the maximum and minimum values are tested. The results from these tests are then analyzed and a general trend for the process should be established. A model should then be fit for the objective function and used to estimate the optimum conditions. Though it requires substantial data analysis, response surface analysis can be a powerful tool when optimizing because it can greatly reduce the time investment, as well as interpret and correlate simulation results without actually running simulations for each changed variable.

The other suggested strategy, lattice search techniques, is broader than response surface analysis. It is typically used for processes involving multiple design variables and consists of three types. The first is an analytical technique that is based on finding the location where gradients of the objective function are zero. This is beneficial when the objective function can be approximated and the number of local extrema is few. However, for most chemical processes, analytical techniques are inadequate as the processes are too complex and do not provide continuous objective functions. The second type of lattice search technique is a response surface strategy similar to the response surface analysis. These are useful and efficient for when the number of design variables and constraints are high and show that the probability that the optimum for the process lies on the end-caps of the variable range. The third technique is the pattern search technique. This technique begins by making an initial optimum value estimation for the key design variable. From there, if the first guess is deemed to be an improvement, additional guesses are made near the first to evaluate the objective function. If the initial guess is shown to degrade the system, then a different direction is followed and analyzed. The strategies for deciding which direction to proceed in and how many iterations to evaluate often stem from the knowledge of the individual unit operations as well as the overall process. The pattern search and response surface of the lattice search techniques are attractive during parametric optimization because they allow the use of discrete variables for discrete optimization. Discrete optimization is the choosing of a small range of variables, evaluating those, determining an optimum from that range and then moving forward to a different set of variables. This does not nearly provide the global optimum of a process, but instead, it demonstrates the variables of highest importance in regards to the objective function.

Optimization of processes can be a complex and rigorous undertaking, but it is vital to many industries. The general procedure can be simplified through the establishment of a base case, then performing topological optimization, followed by parametric optimization using the strategies presented previously. The following section explores the optimization of an ethylbenzene (EB) process in which a base case was referenced while performing topological and parametric optimization using the pattern search technique and discrete optimization.

SECTION II: The Optimization of a Gas-Phase Ethylbenzene Process

The process presented to the group for optimization was the production of EB for use in a styrene plant. Our company, Black Bear Inc., wants to produce the necessary EB instead of purchasing it. To analyze the benefit of producing the EB, we set the NPV as our parameter to maximize. To begin, we simulated a base case that was proposed for the production of EB from ethylene and benzene. The specifications for this product were a production rate of 80,000 tonnes per year of EB, a purity of 99.8 mol% of EB, and no more than 2 parts per million (ppm) of diethylbenzene (DEB) in the product stream. From this basis, we selected different areas of the process that had the potential to be optimized to increase the profit margin. After completing this, we found our NPV to be approximately $76 million, giving us reason to recommend moving forward with the project.

The proposed process included six components in four reactions. The production of EB takes place via the direct addition reaction between ethylene and benzene:

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Ethylene}}{C_2H_4} \rightarrow \underset{\text{Ethylbenzene}}{C_6H_5C_2H_5} \qquad [1]$$

The reaction to produce DEB also occurs:

$$\underset{\text{Ethylbenzene}}{C_6H_5C_2H_5} + \underset{\text{Ethylene}}{C_2H_4} \rightarrow \underset{\text{Diethylbenzene}}{C_6H_4(C_2H_5)_2} \quad [2]$$

Additionally, DEB reacts with excess benzene to form EB:

$$\underset{\text{Diethylbenzene}}{C_6H_4(C_2H_5)_2} + \underset{\text{Benzene}}{C_6H_6} \rightarrow \underset{\text{Ethylbenzene}}{2C_6H_5C_2H_5} \quad [3]$$

Lastly, toluene present in the process reacts with ethylene to produce EB and propylene:

$$\underset{\text{Toluene}}{C_6H_5CH_3} + \underset{\text{Ethylene}}{2C_2H_4} \rightarrow \underset{\text{Ethylbenzene}}{C_6H_5C_2H_5} + \underset{\text{Propylene}}{C_3H_6} \quad [4]$$

Given the components present, we used the SRK-Simsci thermodynamic model in the comprehensive simulator, Pro/II. This model accounts for aromatic hydrocarbons, which our process contains, and most accurately approximates the vapor-liquid-equilibria.

The base case process flow diagram (PFD) can be seen in Figure 2.1. This PFD will be referred to as the “base case” and all optimizations were made with it as the origin.

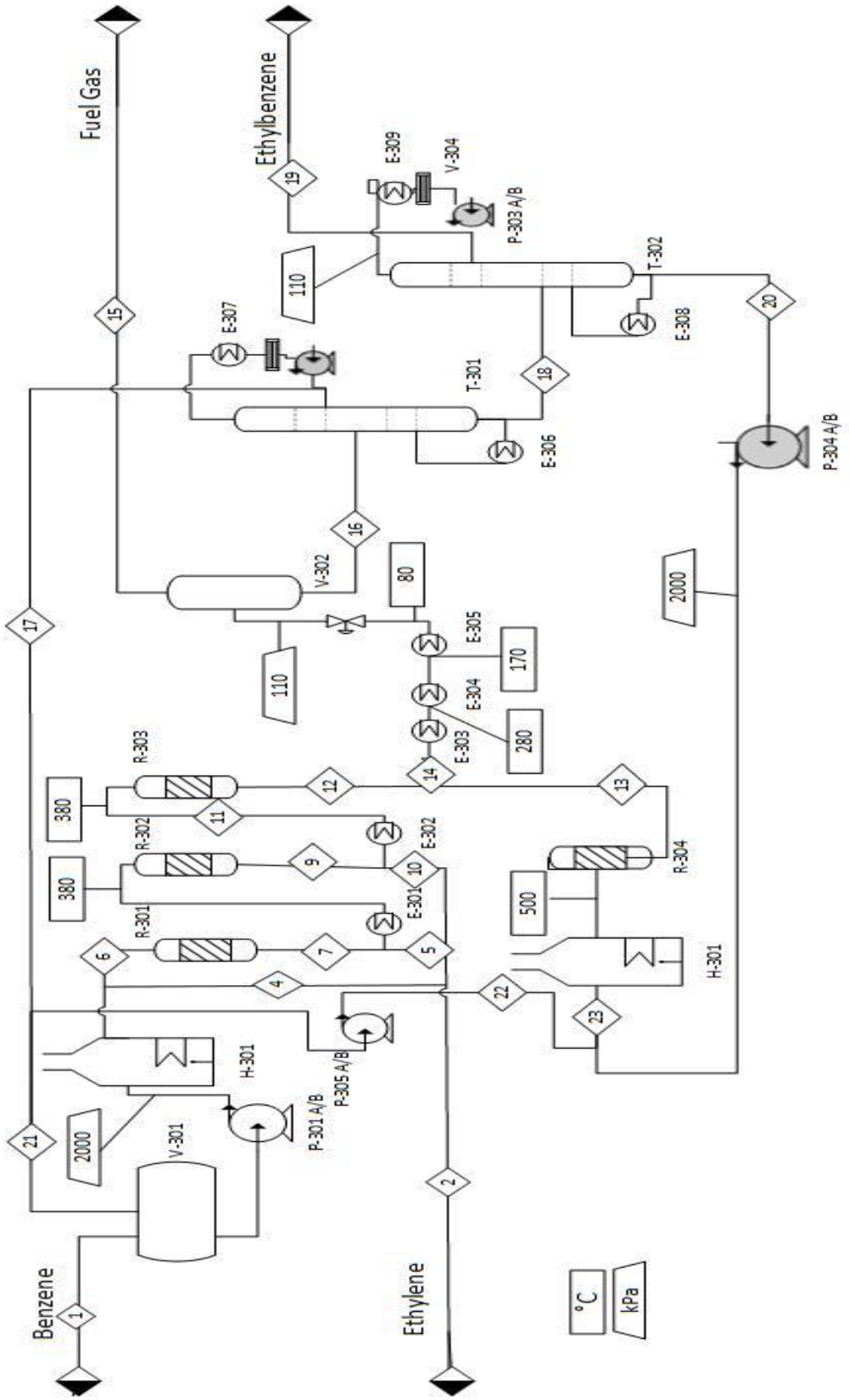


Figure 2.1: Base case process flow diagram for the vapor phase EB production process

When investigating the base case, we determined the NPV for the project to be approximately −$6 million with a minimum accepted rate of return (MARR) of 12%. At this NPV and MARR, the base case process is not recommended for investment. However, while evaluating the base case, we identified numerous areas for improvement that we believed would increase NPV. These areas included the separation section, the reactor section, and potential elimination of the DEB recycle and associated equipment. Based on the evaluation that the project could be improved, we decided to optimize these sections. This was done with the intent to determine how much the NPV could be increased, as well as to make it a profitable project with which to proceed.

Our first area of evaluation for potential optimization was the reactor section. We believed that we could eliminate at least one of the reactors and still achieve the same production. By removing a reactor, there is one less piece of equipment which will lower the fixed capital investment (FCI). We also saw that it might be possible to change the volumes of the reactors without violating the maximum catalyst temperature of 525°C or lowering EB production. Adjusting the reactor volumes would have an effect on equipment cost. Finally, the temperature and pressure into the reactor appeared to be areas that could be evaluated. More efficient reactor operating conditions in regards to desired EB production, should result in an increased NPV.

The second significant area we thought could be improved was the separation section. This consists mainly of the two distillation columns that recycle the benzene and produce the 99.8 mol% EB. It appeared that we would be able to remove the second tower, resulting in a lower overall equipment cost, while still achieving the desired purity and

production of EB. This would also allow us to remove the pump, radiant portion of the fired heater, and fourth reactor that processed the recycle of the undesired DEB. We also realized there was a possibility to optimize the temperature, pressure, and feed tray location of the tower for more efficient operating conditions in order to increase the NPV.

Finally, we noticed there were several smaller portions of the process that had potential for improvement. Included in this was the recovery of benzene and a more efficient heat integration. We saw that there was benzene being lost through the flash vessel and sold as fuel gas, as opposed to being recycled and added to the fresh feed. As for the heat integration, we believed utility costs could be decreased by adjusting the heat exchanger network. By noticing there were many process sections with substantial room for improvement, we decided to move forward with optimizations. Additionally, there were three recommended changes to the overall process that warranted examination, as they had the possibility of increasing NPV.

The first proposed change was the use of a different catalyst. In the base case, catalyst 1, Krypton, was used. However, catalyst 2, Adamantium, advertised suppression of DEB production and had different properties than catalyst 1. Catalyst 1 cost $5/kg and catalyst 2 cost $8/kg, so we recognized that this change in catalysts had the potential to greatly affect our NPV. When we looked at change 1, we chose to examine the selectivity that each catalyst provided through the reactor section of our process. We defined selectivity as the flow rate of EB leaving R-303 divided by the flowrate of DEB leaving R-303. Catalyst 2 had a selectivity three times larger than that of catalyst 1, which was our first indication that this would be the better catalyst. Not only would we have less DEB to

separate from the EB, but we also would not have to feed benzene and ethylene into the first reactor at a ratio of 8:1.

As mentioned above, one of the major benefits of switching to catalyst 2 is that it suppresses the production of DEB, an undesired product. In the base case, R-304 is used to convert DEB to EB through reaction 3. Due to catalyst 2's suppression of DEB, the amount of DEB recycled from the bottoms of T-302 was less than 0.5% of the feed into the tower. We found that the amount of EB produced from reaction 3 did not offset the cost of P-304 A/B, the radiant portion of H-301, and R-304. From this, we were able to eliminate the three previously mentioned pieces of equipment. Additionally, we noticed that the conversion of benzene to EB did not change from R-301 to R-302 to R-303. The purpose of the reactors in series was to increase the conversion of benzene, but this was not occurring, so we removed R-302 and R-303 from the process as well. However, due to the removal of multiple pieces of equipment, when attempting to achieve the product specifications, the volume of the catalyst in R-301 had to be decreased from 20 m^3 to 18 m^3. This was done to avoid a reactor effluent stream over 525 °C, the maximum operating temperature for the catalyst. After implementing the change in catalyst and removing the unnecessary pieces of equipment, our NPV was found to have increased from −$6 million to about −$1.6 million.

Change 2 brought the opportunity to purchase lower grade benzene for the feed. Initially, per base case specifications, the benzene feed was 98 mol% benzene and 2 mol% toluene, purchased for $1.014/kg. The lower grade of benzene feed offered benzene at 90 mol% benzene and 10 mol% toluene for $0.85/kg. To evaluate if this change would be economically beneficial, we implemented the new feed and adjusted the tower specifications to achieve a process that met the three production requirements. After pricing

the process with the new feed, our NPV increased to $65 million, compared to the NPV of −$1.6 million after change 1. No additional changes were required to achieve our desired production. Due to this large jump, we concluded that the new feed was profitable and should be used in further optimizations. One further recommendation for optimization is to test a feed with a larger percentage of toluene at a lower raw material cost, while still checking that product specifications are able to be met. However, that is outside of the scope of this project.

The proposed third change was to separate the toluene from the feed and sell it back to the supplier for $0.91/kg. To evaluate this, we examined the economic potential for our plant. This was done by calculating the amount of EB produced by completely separating out the toluene that was being fed (assuming perfect separation) and comparing it to the amount that could be made by converting the toluene to EB (assuming 100% conversion) and selling all EB produced. Based on this analysis, we found that selling all the toluene via the separation proposed in change 3 would make $8.5 million. If we did not separate the toluene, but rather converted it to EB and sold it, the revenue would be $16 million. This analysis revealed that an increase in NPV as a result of change 3 was unlikely, so it was not further evaluated.

After examining the three different change proposals, we began examining our operating conditions. The first parameter that was evaluated was the reactor bed volume in R-301. Using our base of 18 m^3, we picked points on either side and resized and priced each point. From the points that were tested, we found an optimum at a volume of 19 m^3, which gave us an NPV of $69.3 million. This is an increase of $4.3 million compared to the most recent NPV of $65 million from implementing change 3. All further optimizations in the process were made using a reactor bed volume of 19 m^3.

The next step in our optimization of the reactor was to adjust the temperature exiting the fired heater prior to the reactor. Our base temperature was 400 °C, so we again chose points on either side of this value to evaluate. We did not test a large range outside of the original operating temperature because a higher temperature would cause our reactor to run above the allowable catalyst temperature of 525 °C, and a lower temperature would result in the reactor not producing enough EB. After running the simulation and resizing equipment, we found that our optimum was at the base value of 400 °C, so we used this temperature moving forward.

Finally, we optimized the pressure going into the reactor. To do this, we altered the outlet pressure where our streams of benzene and ethylene meet. Before choosing points, we performed a case study on R-301 to compare the pressure of the reactor to the conversion of benzene through the reactor, with a pressure range from 1850 kPa to 2200 kPa (the maximum operating pressure of the reactor). This graph showed that the conversion increased substantially as pressure increased, but it leveled out just above 2000 kPa. Therefore, we chose three different points to evaluate: 1950 kPa, 2000 kPa, and 2050 kPa. With our analysis, we found that a pressure of 2050 kPa gave the largest NPV of $70.7 million, an increase of $1.4 million.

After optimizing the reactor temperature, pressure, and catalyst volume, we moved to optimization of the separation section of our process. We first started with the towers and began by examining the effect of feed tray location on the NPV. For T-301 (containing a total of 16 trays), we ran a case study to minimize reboiler duty by varying the feed tray location. From the graph produced by the case study, we picked three locations (tray 6, 8, and 12) and evaluated the NPVs for each. The base scenario for feed tray location in T-301 was tray 10 and was determined from the results of the shortcut column. The NPV for feed

tray location of tray 10 was $70.7 million. We found that tray 8 gave the maximum NPV of $71.6 million. We recognize that this is a fairly insignificant increase, however, we found that when fed on tray 6, the reboiler and condenser duties increased significantly and caused the NPV to decrease to $63.5 million. This proved to us that feed tray location and minimizing reboiler and condenser duties did have an impact on the NPV and merited optimization. Additionally, feed tray optimization was something easily achieved through the use of an optimizer in Pro/II.

After examining feed tray location for T-301, we performed a similar case study to the one mentioned above for T-302, which had 22 trays. This case study gave us a few points to evaluate and compare to the initial location of 20, obtained from the shortcut column for T-302. Contrary to our findings for T-301, varying feed tray location for T-302 only returned a one million dollar range in NPV. Though we found an optimum tray location on tray 10, our NPV only increased from $71.6 million to $72.6 million. We recognized that this was a small change, so we did not spend more time attempting to optimize feed tray location in T-302.

After completing our discrete optimization of the reactors and towers, we determined there was the potential to optimize one more section of our process, heat integration. We noticed that a significant yearly cost comes from our utilities, so we looked to minimize this. In our process, we had multiple locations where we were requiring utilities (low pressure steam/high pressure steam) to heat a process stream that was later cooled through use of cooling water. To combat this redundancy, we took the hot process stream out of the reactor at 516 °C and fed it through a new heat exchanger, E-310, that was located directly before H-301. We had two reasons for choosing Stream 8 and the location for where we placed E-310. The first reason was that we recognized that Stream 8 had an

abundance of heat that could be used to heat Stream 3, prior to feeding it to the fired heater. By having E-310 in front of H-301, we were able to significantly decrease the duty required for the fired heater because the crossing of stream 8 and stream 4 allowed for a considerable amount of heat transfer to occur that otherwise would have been done by the fired heater. This had a substantial affect on our NPV because fired heaters are priced off of their duty and we were able to decrease the duty of H-301 from about 20 GJ/hr to 5 GJ/hr. Additionally, because stream 4 was colder than stream 8, it was able to cool stream 8 enough so that we could eliminate E-303 (which was a hot side heat exchanger), which further increased our NPV. Furthermore, the utility requirements for E-304 and E-305 decreased because the temperature difference decreased after making the change. We explored other possibilities for further heat integration, but concluded that the direction we chose was the most feasible with the largest impact on NPV. Prior to heat integration, the NPV was $72 million. After, it increased to $75.5, verifying our choice in heat integration.

Though we recognize at this point in the project that our process is not ready for construction nor is it the final process design, we have been able to optimize many sections of our process. From implementing the change to catalyst 2 and the switch to a lower-grade benzene feed, we were able to remove P-304, R-304, the radiant section of H-301, R-302 and R-303. The elimination of these units resulted in a sizable decrease in the FCI, and therefore a large increase in the NPV. The optimization of R-301 was found to increase the NPV the most at a catalyst volume of 19 m^3, an inlet temperature of 400 °C, and a pressure of 2050 kPa. The optimum feed tray location for T-301 was tray 8 of 16 and tray 21 of 22 in T-302. We recognize that the optimal tray location in T-302 is different from when we optimized feed tray location to our final optimized design, but this is justified as we noticed the tray location did not have a significant impact on NPV. Additionally, the tray location

changed for T-302 due to changing specifications from other units being optimized. Figure 2.2 shows the PFD that represents the optimized vapor phase process.

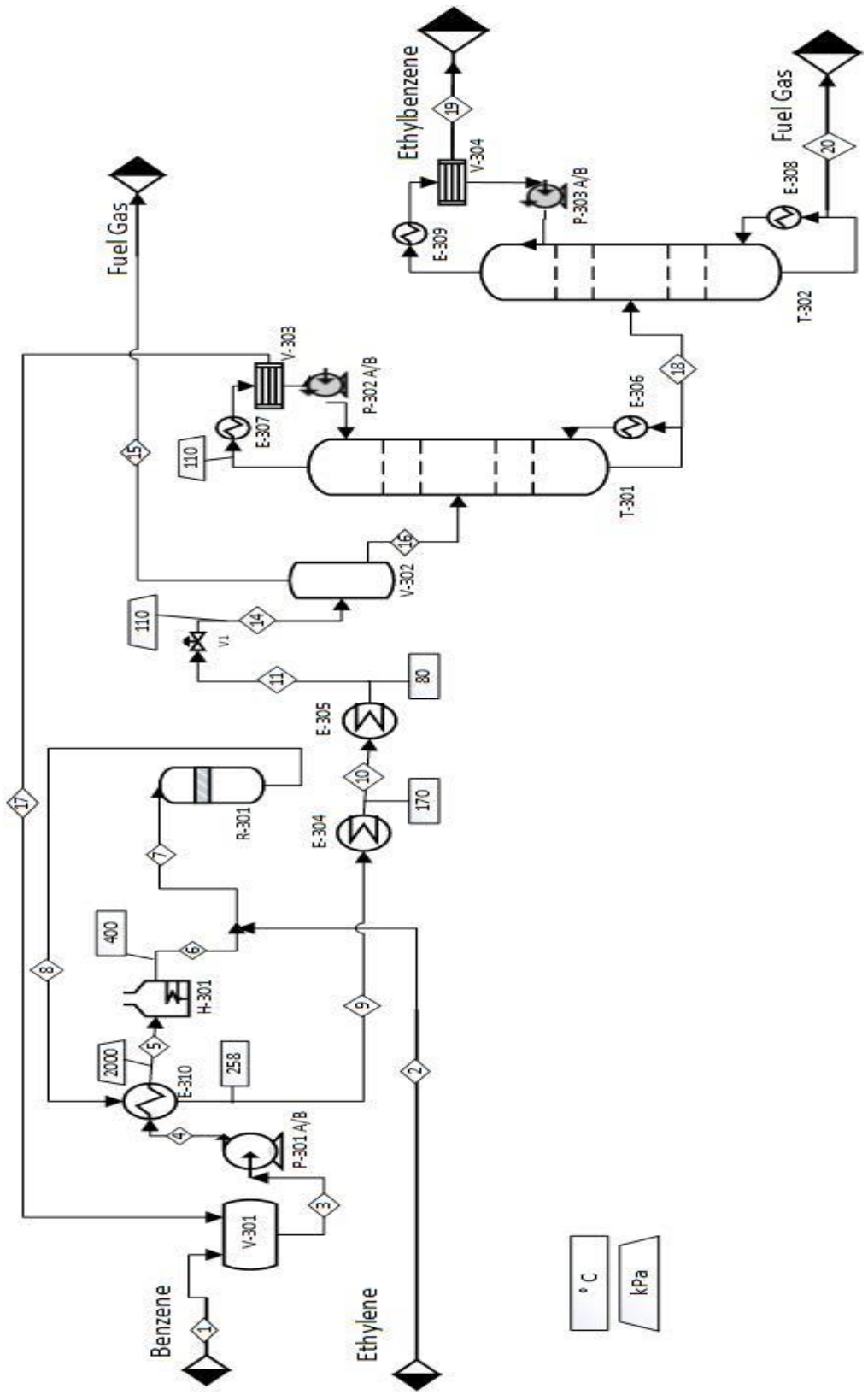


Figure 2.2: Optimized process flow diagram for the vapor phase EB production process

We recommend that this process continue to be improved before proceeding to a final design stage. There are still multiple areas that could be improved that were not investigated in our discrete optimizations. One such investigation might include altering the molar ratio for benzene and ethylene feed into R-301. There are also some additional design considerations that are beyond the scope of what we were evaluating at this stage. For instance, there could be piping or safety concerns in some parts of the process. It is suggested that the proposed changes above be made, but there are still further considerations to address.

Through optimizing different operating conditions within our process, we were able to determine which changes in conditions resulted in the largest impact on NPV. For justification, Figure 2.3 is a graphical representation of NPV per process change and Table 2.1 demonstrates the differences in various economic parameters from each change.

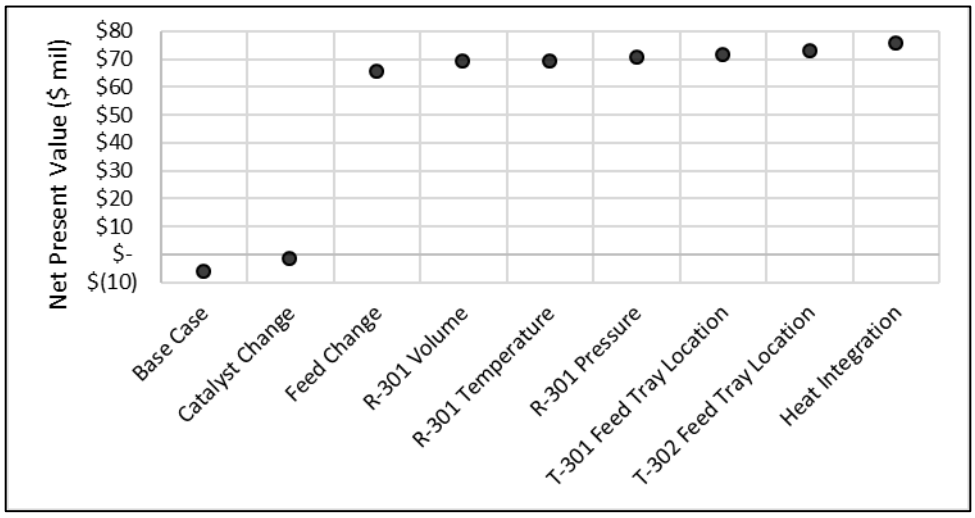


Figure 2.3: NPV Increase for selected changes to the vapor phase EB process

Table 2.1: Economic parameters for selected changes to the vapor phase EB process

	NPV ($ mil)	FCI ($ mil)	EB Breakeven Price	Payback Period (years)
Base Case	-$5.96	$10.82	$1,503.51	8.94
Catalyst Change	-$1.65	$10.64	$1,490.12	6.59
Feed Change	$65.56	$10.98	$1,281.45	1.58
R-301 Volume	$69.25	$10.34	$1,270.00	1.50
R-301 Temperature	$69.25	$10.34	$1,270.00	1.50
R-301 Pressure	$70.73	$10.11	$1,265.42	1.46
T-301 Feed Tray Location	$71.61	$9.97	$1,262.68	1.45
T-302 Feed Tray Location	$72.62	$9.84	$1,259.56	1.43
Heat Integration	$75.53	$8.54	$1,247.82	1.65

As Figure 2.3 and Table 2.1 show, the NPV increases with each optimization. It should also be noted that the x-axis of Figure 2.3 is in chronological order. Additionally, the largest increase in NPV occurs from catalyst change to feed change, with only about a $10 million increase from feed change to heat integration. However, we understand that there are many costs that significantly alter our NPV that are outside of our control. These major costs include the price for EB and the cost of the ethylene feed and benzene feeds. To better understand the relationship between these costs and our NPV, we performed a sensitivity analysis (Figure 2.4) ranging from 70% to 130% of each cost. By far, the price for selling EB had the largest effect on the NPV, showing a range from −$67.5 million to $219.5 million. Additionally, the analysis showed that our NPV was very sensitive to the change in cost of benzene and a slightly less sensitive to the cost of ethylene. The findings from our sensitivity analysis agree with the trends seen in our optimization process, namely, when we implemented change 2 by changing to the less expensive benzene feed, we saw the largest increase in our NPV.

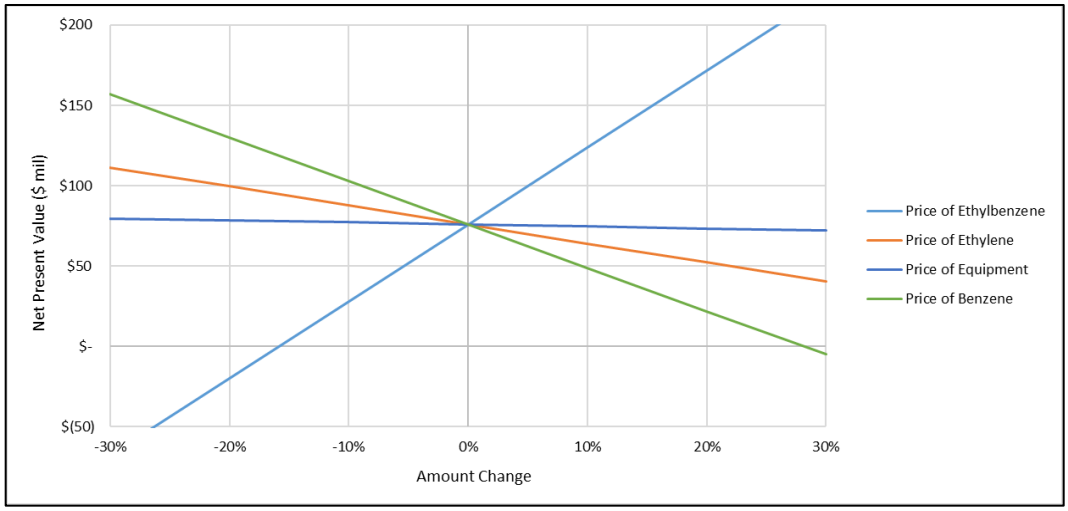


Figure 2.4: Sensitivity analysis for selected variables to the vapor phase EB process

While optimizing the process design was the focus of the project, another important factor that must be considered is safety. Ethane, ethylene, benzene, toluene, and EB are all flammable and require the use of dry chemical powder, carbon dioxide, foam, or fog for extinction if a fire occurs. There is also a need for gas detectors throughout the plant to quickly respond to changes in the composition of volatile organics in the air that could be flammable. When designing, it must be taken into consideration that chemicals must be kept away from sources of ignition. Benzene and its derivatives are known carcinogens and proper safety practices should be followed when handling them. In moving forward with the implementation of the plant, the regulations specific to the state in which the plant will be built should be studied and appropriate safety measures need to be taken. Limiting exposure and release of any of these chemicals is of the utmost importance. To prevent the situation of chemicals abruptly being expelled into the air, there needs to be safety valves installed to shut down when the pressure and/or temperature exceeds the set limit. In order to uphold this preventive measure, routine maintenance and updates to the vessels should be done often. Any chemicals

released to the air could react to become smog and cause health hazards for citizens as well as be absorbed by snow or rain and seep into the ground to cause environmental issues. It is important to prevent this from happening. Most of the chemicals used in this process can be toxic when absorbed through the skin, ingested, or inhaled. Therefore, workers must wear the required safety equipment including safety goggles, gloves, and respiratory protection when handling the process chemicals. Aside from the chemical safety, the heat integration around the reactor potentially poses a hazard. Using the effluent of R-301 to heat the feed can become dangerous and cause a runaway reaction, so tight controls must be implemented to monitor reactor temperature.

After optimizing and considering safety hazards, we recommend moving forward with the project to further examine possible optimizations, such as examining if T-302 could be removed as originally thought. We also recommend looking at the next steps, including, but not limited to, location and plant design.

SECTION III: The Development of a Liquid-Phase Base Case

After the optimization of the gas-phase EB plant from Section II, it was proposed that a similar process be developed for the production of EB using a liquid-phase reaction scheme. Analogous to the optimization portion of the project, the product specifications for the new process are 80,000 tonnes per year of 99.8 mol% EB. Management requested the development of a base case PFD, stream tables, equipment tables, and utility tables upon completion of the investigation into the liquid-phase reaction scheme process. In this section the logic and procedure used to develop the requested material is explained and presented.

In addition to the unchanged product specifications, the three reactions in the system remain the same. These include the reaction between benzene and ethylene to produce EB:

$$C_6H_6 + C_2H_4 \rightarrow C_6H_5C_2H_5 \quad [1]$$

Benzene Ethylene Ethylbenzene

The reaction between EB and ethylene to produce DEB:

$$C_6H_5C_2H_5 + C_2H_4 \rightarrow C_6H_4(C_2H_5)_2 \quad [2]$$

Ethylbenzene Ethylene Diethylbenzene

As well as the reaction between DEB and benzene to produce EB:

$$C_6H_4(C_2H_5)_2 + C_6H_6 \rightarrow 2C_6H_5C_2H_5 \quad [3]$$

Diethylbenzene Benzene Ethylbenzene

Pure benzene is fed to the process, as opposed to the lower grade feed containing toluene as seen in Section 1. For this reason, there is no reaction forming EB from toluene, as

there is no toluene in the process. The reaction kinetics for reaction 1, 2, and 3 can be seen in Appendix 19.

As opposed to optimizing a given process, as was discussed in Section II, this section addresses the development of a base case process that could later be optimized. This generally includes the development of a process concept diagram, a block flow diagram (BFD), a PFD, stream tables, equipment tables, and utility tables, in sequential order. From these diagrams and tables, the majority of information regarding that process can be found.

For the liquid-phase EB process, a process concept diagram (Appendix 18) was first developed. This clearly shows the inputs (benzene, ethylene) and outputs (EB, DEB) for the process and the reactions by which they are formed. From there, a BFD was constructed (Figure 3.1). A BFD shows the major chemical operations, or "blocks", of a chemical process. The major unit operations for the liquid-phase process were similar to that of the gas-phase process, as they were both for the production of EB. From that, it was determined that the process required six blocks, consisting of reactor feed preparation, reactor, separation feed preparation, first separator, second separator, and a recycle. This allowed for the basic overview of the process to be determined, and from there, an initial PFD was constructed based on the units of equipment required for each block. Figure 3.2 shows the finished PFD for the liquid-phase process. It differs slightly from the initial PFD only in that heat exchangers, pumps, and valves were added/removed to aid in separation or the combining of streams.

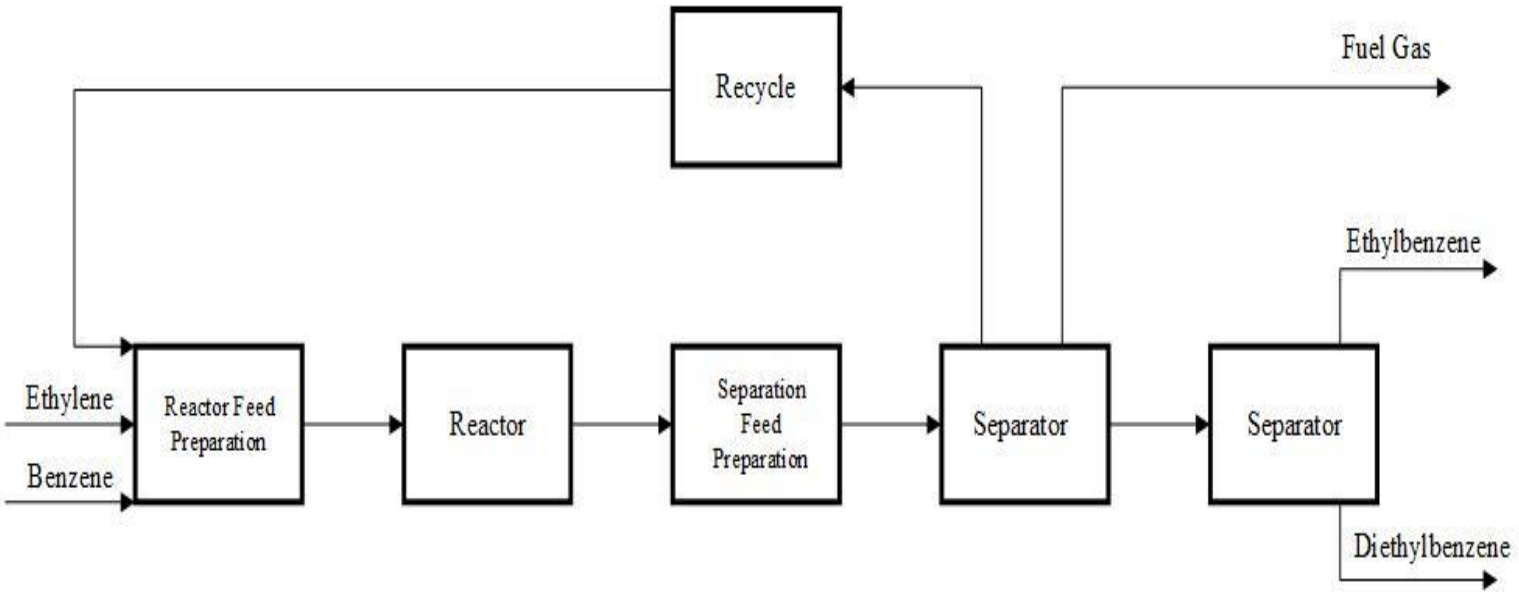


Figure 3.1: Block flow diagram for liquid phase EB production process

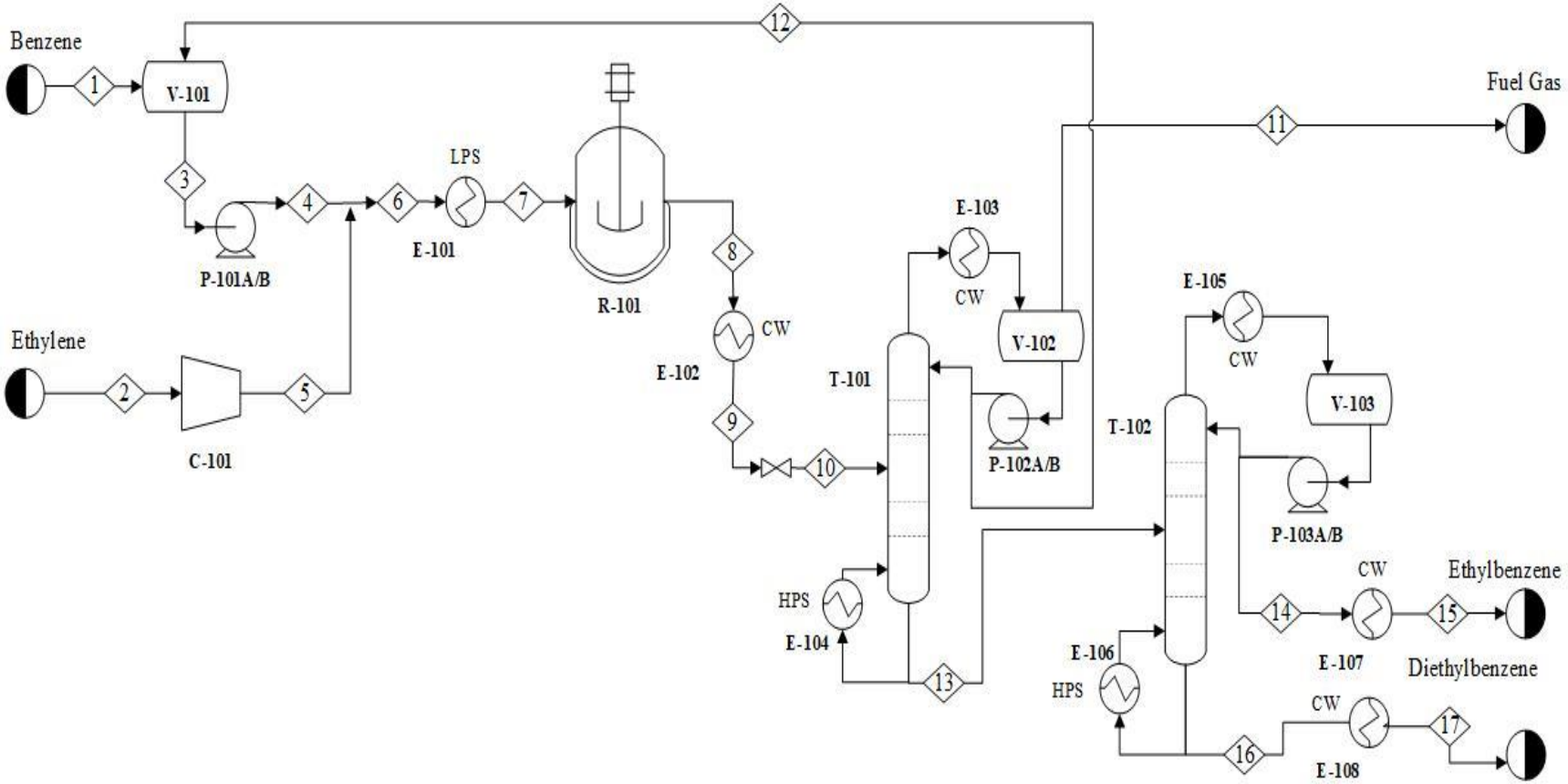


Figure 3.2: Process flow diagram for liquid phase EB production process

The initial PFD was created by using the BFD and selecting the appropriate unit operations for each section. This initial liquid-phase PFD was similar to the gas-phase PFD discussed in Section II. However, the major difference was the type of reactor used in the process. In the vapor-phase process, a packed bed reactor was chosen because catalyst was used. For this process, a continuous-stirred tank reactor (CSTR) was chosen due to the liquid-phase reaction scheme.

After developing a PFD, the next step was to calculate the component flow rates and stream temperatures and pressures for each stream and organize this data into stream tables. These calculations were performed in Excel because there were multiple unknowns and the solver function could be used to find these values based on the design constraints.

In order to formulate the problem in Excel, each of the aforementioned sections of the BFD had to be analyzed sequentially. The reactor feed preparation section, which consists of streams 1 through 7 (Figure 3.2), was addressed first. Calculations for these streams can be seen in Appendix 23. Streams 1 and 2 were pure benzene and ethylene, respectively, both fed at 1 atmosphere (atm) and 25°C. The molar flowrates of streams 1 and 2 were unknown, so these were set as variables in solver. However, equimolar feed quantities were set as a parameter. Stream 3 was the mixing of streams 1 and 12 (the recycle from T-101). The flowrates were additive, but, because the temperature of stream 12 differed from that of stream 2, a new temperature was calculated using the first law of thermodynamics (Appendix 27, Equation 1). The pressure was also 1 atm because both combining streams were at 1 atm. Stream 4 was seen to have the same composition as stream 3 and it was assumed to have a constant temperature over the pump as well. This is a safe assumption because the temperature of a liquid does not increase substantially with

an increase in pressure. The purpose of the pump was to increase the pressure to account for the pressure drop through E-101, as well as raise it to the required pressure for the operating temperature of R-101 to ensure the ethylene remains in the liquid phase (Equation 6 of Appendix 27). Additionally, stream 5 is equivalent to stream 2 in composition, but since ethylene entered the system as a gas, it had to be compressed to match the pressure of stream 4 to allow for safe mixing. Expecting a large increase in temperature due to the rise in pressure, the temperature of this stream was calculated using the thermodynamic relation seen in Appendix 27 (Equation 2). The temperature of the ethylene stream increased from 25°C to 484°C, a 1936% increase. The molar flowrates of streams 4 and 5 were combined to form stream 6, but the mixing of these result in a change in temperature, as stream 5 was much higher than that of stream 4. To determine the temperature, an energy balance was performed with the temperature of stream 6 being the variable in solver. The enthalpy of stream 4 and 5 must equal the enthalpy of stream 6, which was also used as a constraint in solver. The final stream in the reactor feed preparation section was stream 7. As far as composition, it was the same as 6, but the temperature had been decreased to the operating temperature of R-101 (110°C) and there was a 0.2 atm pressure drop over E-101.

After finishing the reactor feed preparation section, I moved forward to the next block in the BFD, the reactor. Though the reactor section only consisted of the inlet and outlet stream, the calculations were much more rigorous than that of the previous block. These can be seen in Appendix 24. First, it was known that a mole balance around the reactor was needed to calculate the outlet concentrations of each component. The general equation for a mole balance is: $In - Out + Generated = Accumulation$. Because the

process was operating at steady state, there was no accumulation, so the equation was set equal to zero and used as a constraint in solver. The in and out terms represent molar flowrate in and molar flowrate out. The generated term is the amount of the reactant consumed (negative generation) in the reaction, as well as the product and by-product formed. To solve the mole balance, the volumetric flowrate of stream 7 was calculated. This was done by assuming constant molar volume and summing the volumetric flowrates of each component. This assumption was not very accurate, because assuming constant molar volume assumes that it is ideal mixing, which is false due to the high operating pressures. However, because this is a preliminary design, assuming constant molar volume simplified the calculations and allowed for an overall base case to be developed. If optimizing this process, more rigorous calculations or a simulator such as Pro/II that has the mathematical capacity to calculate the volumetric flowrate should be used. From the calculated volumetric flowrate, the outlet molar flowrates for each component were found by using guess values for the outlet concentrations. The guess values were unknown variables in solver. We knew the inlet flowrates for R-101, so the only other term we needed to calculate was the generated term. Multiplying the respective rates of reactions for each component by the volume of the reactor, 150 m^3, accomplished this. The rates of reactions were calculated using the reaction kinetics found in Appendix 19 and the operating temperature of the reactor, 110°C. The calculations for reaction rates can be seen in Appendix 24. Once the generated term was calculated, the mole balance was set to 0 in solver by changing the outlet concentration of each component. After the base case stream table was solved, the conversion of ethylene out of R-101 was 98% (Appendix 27, Equation 3).

After setting up the equations for the reactor block of the BFD, I moved to the separation feed preparation. Calculations for which can be seen in Appendix 25. To prepare the process for separation in T-101, the effluent from the reactor was cooled, and the pressure was lowered. In theory, by lowering the pressure, better separation is achieved because the lower pressure exacerbates the difference in the relative volatilities of the light and heavy keys. A material balance on stream 9 was performed to determine the amount of liquid and vapor of each component in the stream, as well as to calculate the temperature out of E-102. To perform the material balance, the vapor pressure of each component in stream 10 was calculated. This was done through Antoine's Equation (Appendix 27, Equation 4) and referencing the temperature of stream 9 and using it as an unknown in solver. Once the component vapor pressures were calculated, the vapor phase mole fractions were calculated using Raoult's Law (Appendix 27, Equation 5) and then used to find the molar flowrate of vapor for each component in stream 9. The liquid molar flowrates, liquid mole fractions and overall liquid flowrate were found by setting them as variables in solver and using the material balance to set the difference between the total flowrate of 9, the liquid portion, and vapor portion equal to zero. From this, an energy balance was performed around the valve to determine the bubble point temperature of stream 10.

After the separation feed preparation portion of the process, I calculated the stream compositions, temperatures, and pressures for the two separator blocks and the recycle block of the BFD as seen in Appendix 25 and 26. For the first separator, T-101, the project specifications were that the recovery of benzene to the distillate was to be 99.95% and the recovery of EB to the bottoms was to be 99.9%. A mole balance was executed around the

tower to determine the amount of liquid in the distillate, which included stream 11, the fuel gas, and stream 12, the benzene recycle. Stream 13, the bottoms of T-101 and feed for T-102, was determined from the recovery specifications. Additionally, it was assumed that nothing lighter than the light key would leave in the bottoms and nothing heavier than the heavy key would leave in the distillate. This meant that all the ethylene left via the distillate, because benzene was the light key. To determine the composition of the fuel gas stream, Antoine's Equation and Raoult's Law were used to find the component vapor pressures and the vapor fraction of the stream, in a similar manner as discussed for the separation feed preparation. The benzene recycle was calculated by changing the mole fractions of the stream, as variables in solver, while using the mole balance as a constraint. The temperature of the bottoms, stream 13, was calculated using Antoine's Equation to find the vapor pressures of each component in the stream and then Raoult's Law to determine the vapor fractions in the stream. This was used as a constraint in solver to set the sum of the vapor fractions equal to one while solving for the temperature. For the second separator block, T-102, the recovery specifications differed slightly from those of T-301 such that the recovery of EB to the distillate, stream 14, was 99.9% and the recovery of DEB to the bottoms, stream 16, was 99.99%. As for finding the temperatures for each of those streams, the same process of using Antoine's Equation and Raoult's Law for stream 13 was followed.

After analyzing each section of the BFD and adhering to the product specifications and design constraints, solver was used to determine the temperatures, pressures, and component molar flowrates of each stream, as can be seen in Figure 3.3.

Figure 3.3: Stream tables for the liquid phase EB production process

	1	**2**	**3**	**4**	**5**	**6**
Temperature (°C)	25.0	25.0	57.9	57.9	483.5	147.4
Pressure (atm)	1.0	1.0	1.0	54.8	54.8	54.8
Total (kmol/hr)	112.1	112.1	328.2	328.2	112.1	440.3
Total (kg/hr)	8759.7	3145.7	25624.8	25624.8	3145.7	28770.5
Molar Flowrates (kmol/hr)						
Ethylene		112.1	0.3	0.3	112.1	112.4
Benzene	112.1		327.8	327.8		327.8
Ethylbenzene			0.1	0.1		0.1
Diethylbenzene						

	7	**8**	**9**	**10**	**11**	**12**
Temperature (°C)	110.0	110.0	89.0	89.0	75.0	75.0
Pressure (atm)	54.6	54.6	54.4	2.0	1.0	1.0
Total (kmol/hr)	440.3	330.3	330.3	330.3	13.9	216.0
Total (kg/hr)	28770.5	28751.7	28751.7	28751.7	980.6	16865.1
Molar Flowrates (kmol/hr)						
Ethylene	112.4	2.3	2.3	2.3	2.1	0.3
Benzene	327.8	227.6	227.6	227.6	11.8	215.7
Ethylbenzene	0.1	90.5	90.5	90.5	0.0	0.1
Diethylbenzene		9.9	9.9	9.9		0.0

	13	**14**	**15**	**16**	**17**
Temperature (°C)	149.0	143.0	50.0	200.2	50.0
Pressure (atm)	1.3	1.2	1.0	1.5	1.3
Total (kmol/hr)	100.3	90.4	90.4	9.9	9.9
Total (kg/hr)	10906.0	9594.8	9594.8	1311.2	1311.2
Molar Flowrates (kmol/hr)					
Ethylene					
Benzene	0.1	0.1	0.1		
Ethylbenzene	90.4	90.3	90.3	0.1	0.1
Diethylbenzene	9.9	0.0	0.0	9.8	9.8

From the calculated information, the appropriate equipment and utility data for the process was determined and tabulated in Appendix 22. Through compilation of the stream tables, equipment and utility tables, and a finalized PFD, a base case of a liquid-phase EB process that produces 80,000 tonnes per year of 99.8 mol% EB was developed. From here, the base case can be optimized, determined if profitable, and returned to management.

SECTION IV: Conclusion to the Development and Optimization of an Ethylbenzene Process

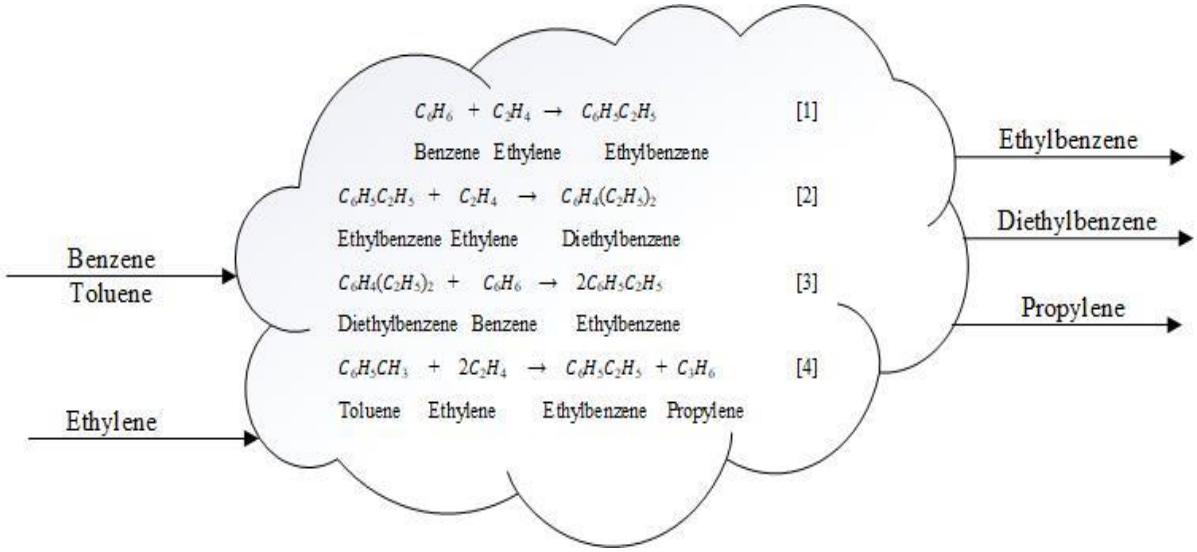
The purpose of this thesis was to apply the knowledge gained during the undergraduate years of Chemical Engineering to an industrial and real-life example. This was done specifically by examining an ethylbenzene process.

First, a vapor phase EB process was optimized from its base case with the objective of maximizing NPV. This was achieved through topological and parametric optimizations and the use of a Pro/II simulator. Multiple unit operations were analyzed to determine the local optimum for each. Upon completion of the optimization of the vapor phase EB process, it was determined that the NPV increased from a starting value of −$6 million to an optimized value of $76 million.

Second, a liquid phase EB process was developed from a process description. This was accomplished by creating a BFD and PFD, followed by the completion of stream, equipment, and utility tables. The largest focus for this portion was the calculations of each component flowrate, temperature, and pressure for each stream. The calculations were done in Excel with the use of specific equations and relations such as Raoult's Law, Antoine's Equation, and the first law of thermodynamics. By successfully developing a PFD and stream tables, it was shown that a liquid phase process for the production of EB was feasible. This process could further be optimized in a similar manner as the liquid phase EB process.

APPENDIX TABLE OF CONTENTS

Appendix 1: Process Concept Diagram for Vapor Phase EB Process



Appendix 2: Reactions and Reaction Kinetics for Section II

Reactions:

$$C_6H_6 + C_2H_4 \rightarrow C_6H_5C_2H_5 \quad [1]$$
benzene ethylene ethylbenzene

$$C_6H_5C_2H_5 + C_2H_4 \rightarrow C_6H_4(C_2H_5)_2 \quad [2]$$
ethylbenzene ethylene 1,4-diethylbenzene

$$C_6H_4(C_2H_5)_2 + C_6H_6 \rightarrow 2C_6H_5C_2H_5 \quad [3]$$
1,4-diethylbenzene benzene ethylbenzene

$$C_6H_5CH_3 + 2C_2H_4 \rightarrow C_6H_5C_2H_5 + C_3H_6 \quad [4]$$
toluene ethylene ethylbenzene propylene

Reaction Kinetics Rate Law:

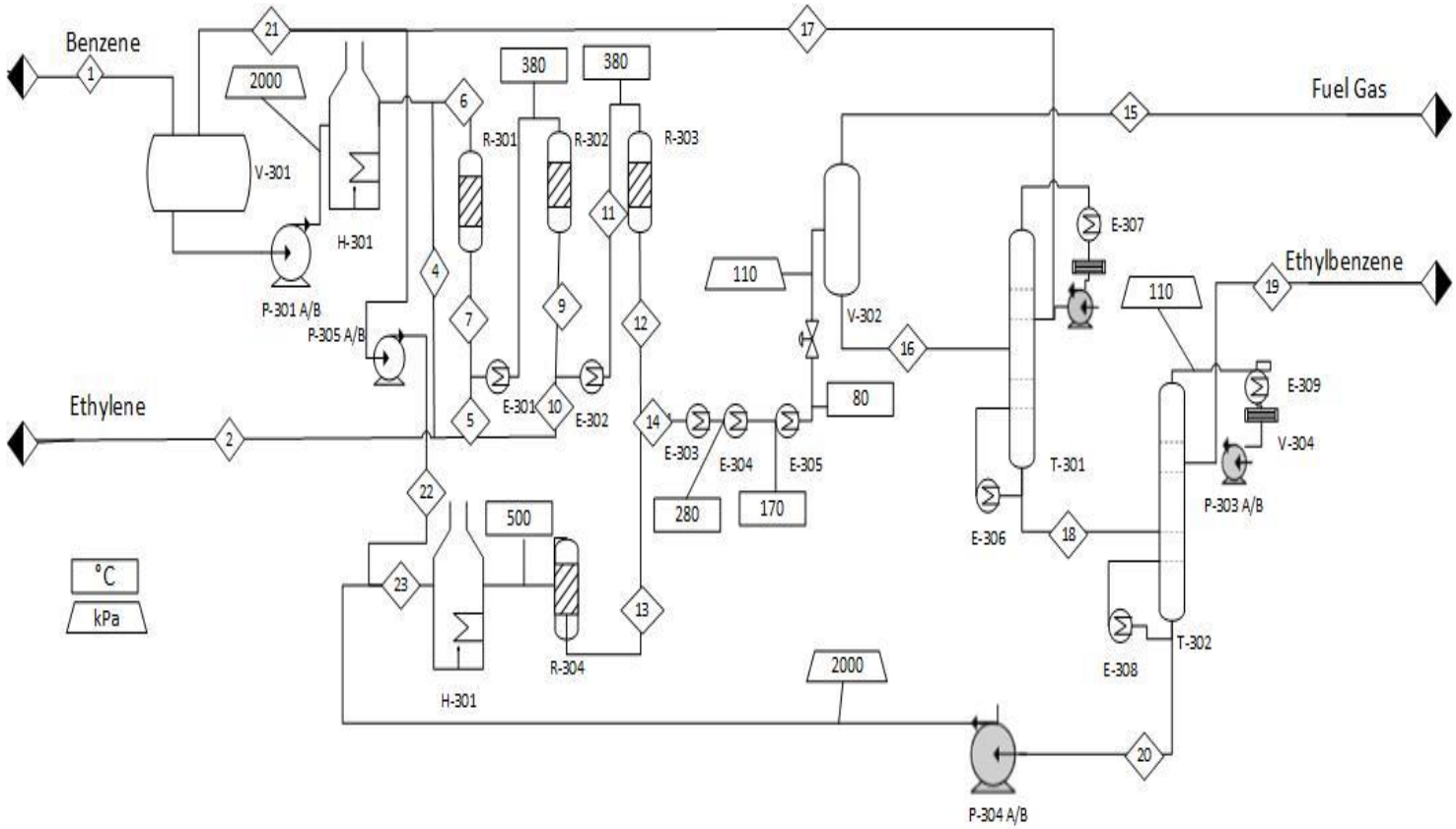
$$-r_i = k_{0,i}e^{-E_i/RT}C^a_{ethylene}C^b_{EB}C^c_{toluene}C^d_{benzene}C^e_{DEB}$$

Catalyst 1 (Krypton) Reaction Kinetics

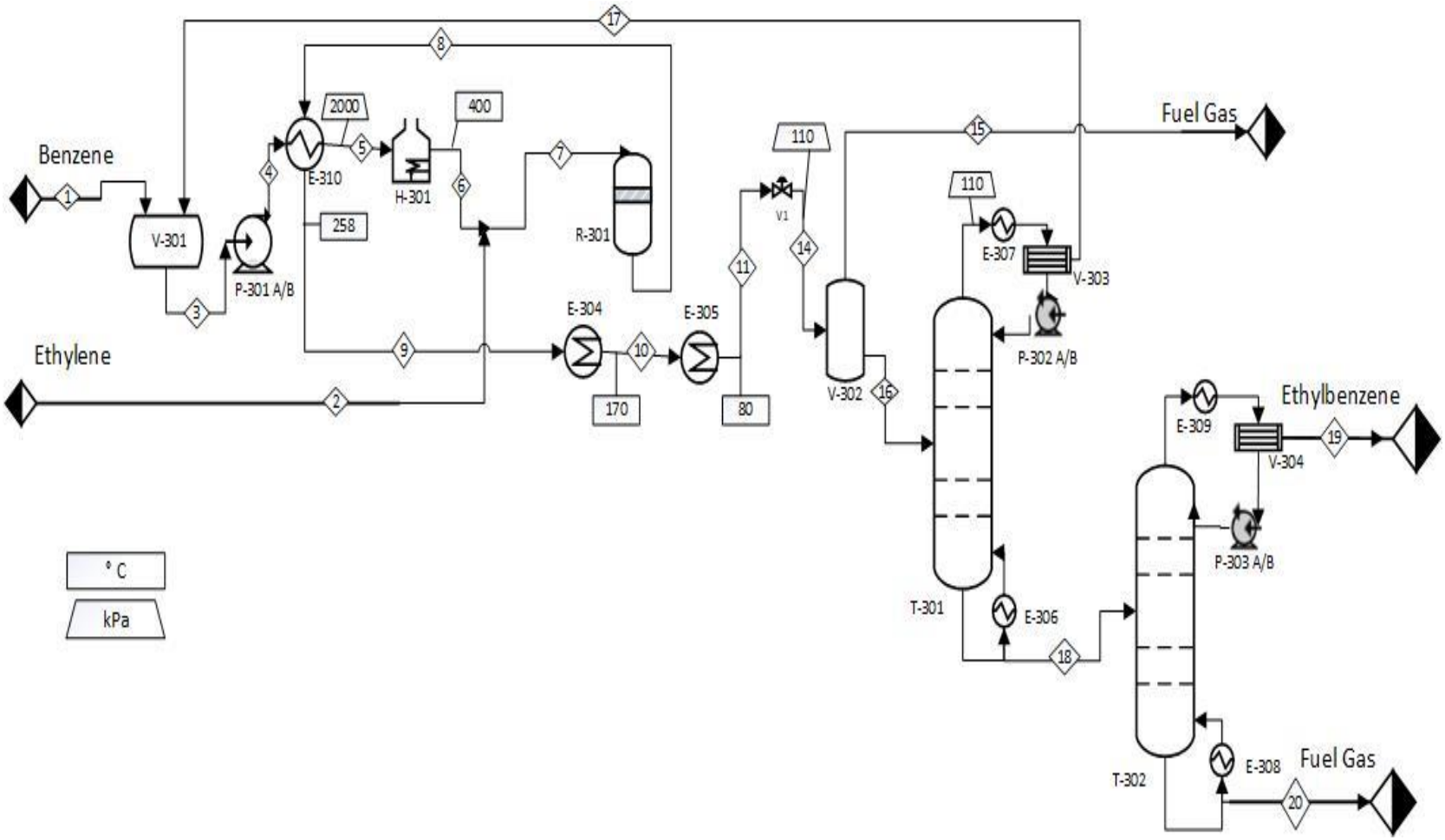
i	***E_i*** **(kcal/kmol)**	***$k_{0,i}$***	***a***	***b***	***c***	***d***	***e***
1	22,500	1.00×10^6	1	0	0	1	0
2	22,500	6.00×10^5	1	1	0	0	0
3	25,000	7.80×10^6	0	0	0	1	1
4	20,000	3.80×10^8	2	0	1	0	0

Catalyst 2 (Adamantium) Reaction Kinetics

i	***E_i*** **(kcal/kmol)**	***$k_{0,i}$***	***a***	***b***	***c***	***d***	***e***
1	22,500	1.50×10^6	1	0	0	1	0
2	22,500	1.00×10^5	1	1	0	0	0
3	25,000	7.80×10^6	0	0	0	1	1
4	20,000	3.80×10^8	2	0	1	0	0



Appendix 3: Base Case Process Flow Diagram for Section II



Appendix 4: Optimized Case Process Flow Diagram for Section II

Appendix 5: Optimized Stream Flow Table, Utility, and Equipment Summary for Section II

Table 5.1: Stream Flow Table

Stream No.	**1**	**2**	**3**	**4**	**5**	**6**
Temp °C	25.0	25.0	35.8	36.2	259.0	400.0
Pres kPa	110.0	2000.0	110.0	2000.0	2000.0	1985.0
Vapor mole Fraction	0	1	0	0	1	1
Total kmol/h	94.5	101.4	232.4	232.4	232.4	232.4
Total kg/h	7514.3	2859.1	18337.3	18337.5	18337.5	18337.5
Flowrates in kmol/h						
Ethylene		94.3				
Ethane		7.1	0.8	0.8	0.8	0.8
Propylene			3.1	3.1	3.1	3.1
Benzene	85.1		211.9	211.9	211.9	211.9
Toluene	9.5		9.5	9.5	9.5	9.5
Ethylbenzene			7.2	7.2	7.2	7.2
1,4-DiEthylBenzene			1.1E-07	1.1E-07	1.1E-07	1.1E-07

Stream No.	**7**	**8**	**9**	**10**	**11**	**14**
Temp °C	349.1	521.3	258.0	170.0	80.0	66.8
Pres kPa	2050.0	2029.6	2029.6	2029.6	2029.6	110.0
Vapor mole Fraction	1	1	1	0	0	0
Total kmol/h	333.8	249.0	249.0	249.0	249.0	249.0
Total kg/h	21196.6	21196.4	21196.4	21196.4	21196.4	21196.4
Flowrates in kmol/h						
Ethylene	94.3	0.1	0.1	0.1	0.1	0.1
Ethane	7.9	7.9	7.9	7.9	7.9	7.9
Propylene	3.1	12.5	12.5	12.5	12.5	12.5
Benzene	211.9	136.6	136.6	136.6	136.6	136.6
Toluene	9.5					
Ethylbenzene	7.2	91.9	91.9	91.9	91.9	91.9
1,4-DiEthylBenzene	1.1E-07	0.02	0.02	0.02	0.02	1.5E-02

Table 5.1: Stream Flow Table (cont'd)

Stream No.	**15**	**16**	**17**	**18**	**19**	**20**
Temp °C	66.8	66.8	43.1	141.8	138.5	152.7
Pres kPa	110.0	110.0	110.0	120.0	110.0	140.0
Vapor mole Fraction	1	0	0	0	0	0
Total kmol/h	27.4	221.6	137.9	83.7	83.6	0.1
Total kg/h	27.4	221.6	137.9	83.7	83.6	0.1
Flowrates in kmol/h						
Ethylene	0.1					
Ethane	7.1	0.8	0.8			
Propylene	9.5	3.1	3.1			
Benzene	9.7	126.9	126.8	0.1	0.1	
Toluene						
Ethylbenzene	1.1	90.8	7.2	83.6	83.6	0.1
1,4-DiEthylBenzene	3.1E-05	1.5E-02	1.1E-07	1.5E-02	1.6E-04	1.5E-02

	Rigorous Columns (Streams Referenced)				
Stream No.	**16__**	**17__**	**18__**	**19__**	**20__**
Temp °C	66.8	39.6	141.7	138.4	149.2
Pres kPa	110.0	110.0	120.0	110.0	140.0
Vapor mole Fraction	0	0	0	0	0
Total kmol/h	221.6	130.7	90.9	90.6	0.3
Total kg/h	221.6	130.7	90.9	90.6	0.3
Flowrates in kmol/h					
Ethylene					
Ethane	0.8	0.8			
Propylene	3.1	3.1			
Benzene	126.9	126.7	0.2	0.2	
Toluene					
Ethylbenzene	90.8	0.1	90.7	90.4	0.3
1,4-DiEthylBenzene	1.5E-02	1.2E-10	1.5E-02	1.8E-04	1.5E-02

Table 5.2: Utility Summary

Stream Name	bfw to E-304	cw to E-305	lps to E-306	cw to E-307	hps to E-308	cw to E-309
Temp °C	115	30	160	30	254	30
Pressure kPa	600	400	600	400	4200	400
Flowrate in 10^3 kg/h	3.92	111.91	4.34	198.47	2.28	132.55
Duty (GJ/h)	9.09	4.06	9.24	-8.30	5.47	-5.54

Table 5.3: Equipment Specifications Summary

Heat Exchangers	
E-304 1-2 exchanger,fixed head, carbon steel process stream in tubes Q = 9.51 GJ/h maximum pressure rating of 2,200 kPa	**E-305** 1-2 exchanger, floating head, carbon steel process stream in tubes Q = 4.06 GJ/h maximum pressure rating of 2,200 kPa
E-306 1-2 exchanger, kettle reboiler, carbon steel process stream in shell Q = 9.24 GJ/h maximum pressure rating of 200 kPa	**E-307** 1-2 exchanger, floating head, carbon steel process stream in shell Q = 8.30 GJ/h maximum pressure rating of 200 kPa
E-308 1-2 exchanger, kettle reboiler, carbon steel process stream in shell Q = 5.47 GJ/h maximum pressure rating of 200 kPa	**E-309** 1-2 exchanger, floating head, carbon steel process stream in shell Q = 5.54 GJ/h maximum pressure rating of 200 kPa
E-310 1-2 exchanger, floating head, carbon steel process stream in tubes Q = 13.29 GJ/h maximum pressure rating of 4,200 kPa	

Pumps	
P-301 A/B Carbon steel - positive displacement Efficiency 75%	**P-302 A/B** Carbon steel - positive displacement Efficiency 75%
P-303 A/B Carbon steel - positive displacement Efficiency 75%	

Fired Heater	
H-301 75% thermal efficiency maximum pressure rating of 2,200 kPa	

Reactor	
R-301 stainless steel packed bed, ZSM-5 mol. Sieve catalyst V_{bed} = 19 m^3 maximum pressure rating of 2,200 kPa Maximum allowable catalyst temperature = 525°C	

Table 5.3: Equipment Specifications Summary (cont'd)

Vessels	
V-301 21.4 m^3 Carbon steel Maximum operating pressure = 250 kPa horizontal	**V-302** 8.0 m^3 Carbon steel Maximum operating pressure = 250 kPa vertical
V-303 2.7 m^3 Carbon steel Maximum operating pressure = 300 kPa horizontal	**V-304** 2.4 m^3 Carbon steel Maximum operating pressure = 250 kPa horizontal

Towers	
T-301 Carbon steel 60% efficient trays 0.5 m tray spacing maximum pressure rating of 300 kPa	**T-302** Carbon steel 60% efficient trays 0.5 m tray spacing maximum pressure rating of 300 kPa

Appendix 6: Equipment and Investment Cost for Optimized Case of Section II

ID	E-304	E-305	E-306	E-307	E-308	E-309	E-310	H-301
Material	CS	CS	CS	CS	CS	CS	CS	SS
K_1	4.3247	4.8306	4.4646	4.8306	4.4646	4.8306	4.8306	7.3488
K_2	-0.3030	-0.8509	-0.5277	-0.8509	-0.5277	-0.8509	-0.8509	-1.1666
K_3	0.1634	0.3187	0.3955	0.3187	0.3955	0.3187	0.3187	0.2028
Min	10	10	10	10	10	10	10	1000
Max	1000	1000	1000	1000	1000	1000	1000	100000
A req	Area	Area	Area	Area	Area	Area	Area	Duty
Units	m^2	m^2	m^2	m^2	m^2	m^2	m^2	kW
Spares	0	0	0	0	0	0	0	0
Ht (m)	-	-	-	-	-	-	-	-
D (m)	-	-	-	-	-	-	-	-
Theoretical Power	-	-	-	-	-	-	-	1558.4
Efficiency	-	-	-	-	-	-	-	75%
A or P	23.3	39.1	81.5	555.0	48.3	24.8	234.6	2493.4
C_p^0	$16,435.74	$19,222.31	$79,532.41	$78,644.43	$49,788.98	$18,356.36	$40,210.18	$532,168.77
Shell P (barg)	5.6	20.1	0.3	0.2	0.5	0.2	0.2	21.0
Tube P (barg)	20.1	3.4	5.6	3.4	45.2	3.4	3.4	-
Op P	-	-	-	-	-	-	-	-
C_1	-0.00164	0.03881	-0.00164	-0.00164	-0.00164	-0.00164	-0.00164	0.1347
C_2	-0.00627	-0.11272	-0.00627	-0.00627	-0.00627	-0.00627	-0.00627	-0.2368
C_3	0.0123	0.08183	0.0123	0.0123	0.0123	0.0123	0.0123	0.1021
F_p	1.03	1.07	1	1	1.05	1	1	1.0
B_1	1.63	1.63	1.63	1.63	1.63	1.63	1.63	-
B_2	1.66	1.66	1.66	1.66	1.66	1.66	1.66	-
F_m	1	1	1	1	1	1	1	2.05
F_q	-	-	-	-	-	-	-	-
F_{BM} BASE	3.3	3.3	3.3	3.3	3.3	3.3	3.3	2.8
F_{BM}	3.3	3.4	3.3	3.3	3.4	3.3	3.3	2.8
C_{BM}^0 BASE	$54,073.57	$63,241.40	$261,661.63	$258,740.18	$163,805.74	$60,392.41	$132,291.51	$1,490,072.57
C_{BM} 2001	$54,892.07	$65,475.04	$261,661.63	$258,740.18	$167,938.22	$60,392.41	$132,291.51	$1,490,402.71
C_{BM} 2020	$77,177.97	$92,057.57	$367,894.93	$363,787.38	$236,120.29	$84,911.43	$186,001.19	$2,095,498.66

Appendix 6 (cont'd): Equipment and Investment Cost for Optimized Case

ID	P-301 A/B	P-302 A/B	P-303 A/B	V-301	V-302	V-303	V-304
Material	CS	CS	CS	CS	CS	CS	CS
K_1	3.4771	3.3892	3.3892	3.5565	3.4974	3.5565	3.5565
K_2	0.1350	0.0536	0.0536	0.3776	0.4485	0.3776	0.3776
K_3	0.1438	0.1538	0.1538	0.0905	0.1074	0.0905	0.0905
Min	1	1	1	0	0	1	0
Max	100	300	300	628	520	50	628
A req	Shaft Power	Shaft Power	Shaft Power	Volume	Volume	Volume	Volume
Units	kW	kW	kW	m^3	m^3	m^3	m^3
Spares	1	1	1	0	0	0	0
Ht (m)	-	-	-	0	0	0	0
D (m)	-	-	-	0	0	0	0
Theoretical Power	11.2407	-	-				
Efficiency	0.75	0.75	0.75				
A or P	15.0	1.0	1.0	21.4	8.0	2.7	2.4
C_p^0	$13,665.80	$4,900.38	$4,900.38	$16,564.65	$9,738.35	$5,452.42	$5,169.13
Shell P (barg)	21.0	0.2	0.2	1.8	1.8	1.8	1.8
Tube P (barg)	-	-	-	-	-	-	-
Op P	-	-	-	3.5	3.5	3.5	3.5
C_1	-0.245382	0	0	-	-	-	-
C_2	0.259016	0	0	-	-	-	-
C_3	-0.01363	0	0	-	-	-	-
F_p	1.183763968	1	1	1.379584018	1.132358774	1	1
B_1	1.89	1.89	1.89	1.49	2.25	1.49	1.49
B_2	1.35	1.35	1.35	1.52	1.82	1.52	1.52
F_m	1.4	1.58	1.58	1	1	1	1
F_q	-	-	-	-	-	-	-
F_{BM} BASE	3.8	4.0	4.0	3.0	4.1	3.0	3.0
F_{BM}	4.1	4.0	4.0	3.6	4.3	3.0	3.0
C_{BM}^0 BASE	$51,656.74	$19,714.24	$19,714.24	$49,859.60	$39,635.08	$16,411.77	$15,559.07
C_{BM} 2001	$56,403.06	$19,714.24	$19,714.24	$59,416.87	$41,980.98	$16,411.77	$15,559.07
C_{BM} 2020	$79,302.42	$27,718.12	$27,718.12	$83,539.82	$59,025.04	$23,074.87	$21,875.98

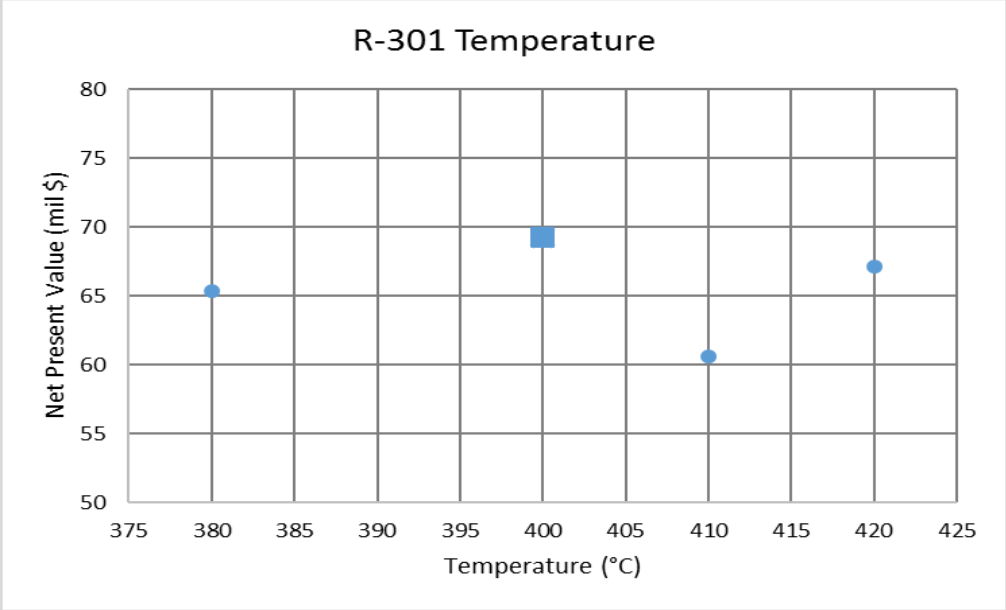
Appendix 6 (cont'd): Equipment and Investment Cost for Optimized Case

ID	R-301	T-301	T-302	Trays 301	Trays 302
Material	SS	CS	CS	CS	CS
K_1	3.4974	3.4974	3.4974	2.9949	2.9949
K_2	0.4485	0.4485	0.4485	0.4465	0.4465
K_3	0.1074	0.1074	0.1074	0.3961	0.3961
Min	0	0	0	0	0
Max	520	520	520	12	12
A req	Volume	Volume	Volume	area	area
Units	m^3	m^3	m^3	m^2	m^2
Spares	0	0	0	0	0
Ht (m)	0	0	0	0	0
D (m)	0	0	0	0	0
Theoretical Power					
Efficiency					
A or P	23.5	38.1	33.6	2.6	1.8
C_p^0	$20,612.36	$29,819.66	$27,043.29	$1,784.81	$1,347.82
Shell P (barg)	21.2	1.9	2.1	-	-
Tube P (barg)	-	-	-	-	-
Op P	23.32	3.6	3.8	-	-
C_1	-	-	-	0	0
C_2	-	-	-	0	0
C_3	-	-	-	0	0
F_p	4.337943722	1.287734588	1.174683066	1	1
B_1	2.25	2.25	2.25	-	-
B_2	1.82	1.82	1.82	-	-
F_m	3.1	1	1	-	-
F_q	-	-	-	1	1
F_{BM} BASE	7.9	4.1	4.1	1.0	1.0
F_{BM}	26.7	4.6	4.4	1.0	1.0
C_{BM}^0 BASE	$162,672.76	$121,366.02	$110,066.19	$1,784.81	$1,347.82
C_{BM} 2001	$550,858.75	$136,981.89	$118,663.88	$42,835.42	$44,478.12
C_{BM} 2020	$774,504.61	$192,595.84	$166,840.82	$60,226.38	$62,536.01

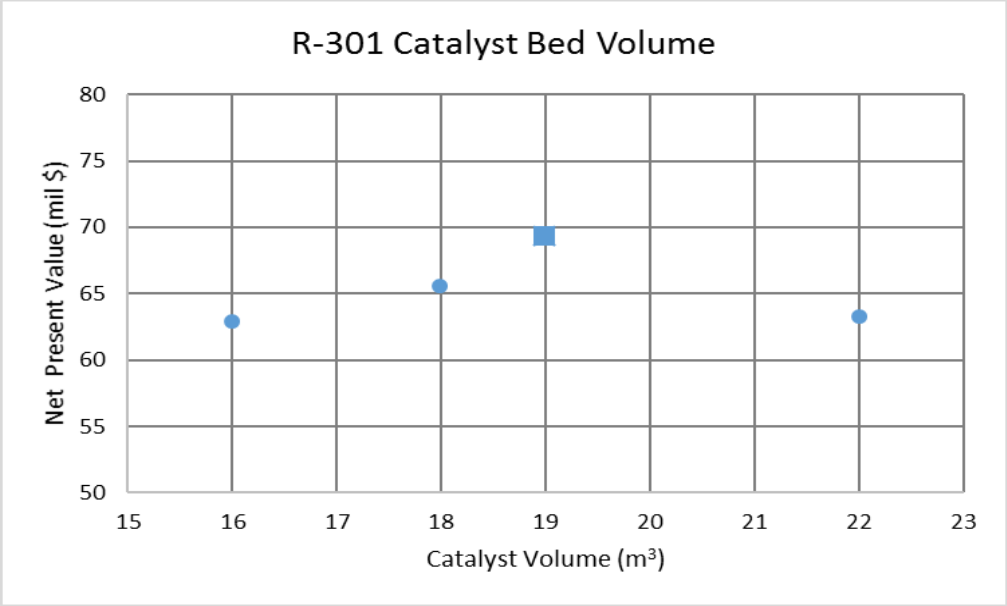
Appendix 6 (cont'd): Equipment and Investment Cost for Optimized Case

2001 Cost Index	397
2016 Cost Index	536.4
CEPCI	558.2
	$M
Total Base C_{BM}	3.61
CEPCI Adjusted C_{BM}	5.08
Total Module Cost	5.99
Grass Roots Cost (FCI)	8.54
Grass Roots with Building and Land	14.04

Appendix 7: Reactor Optimization and Pressure Case Study for Section II

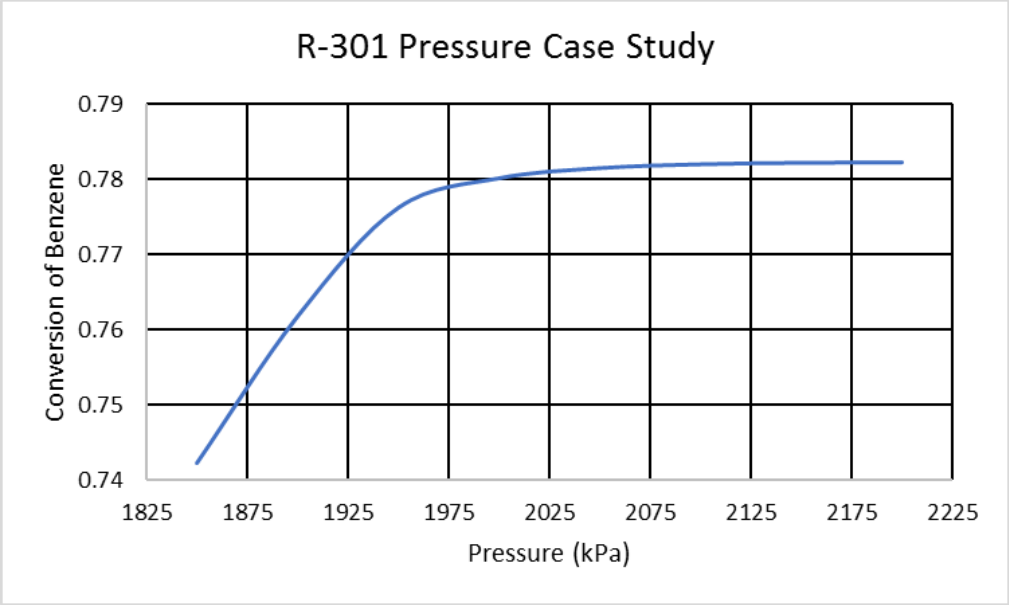


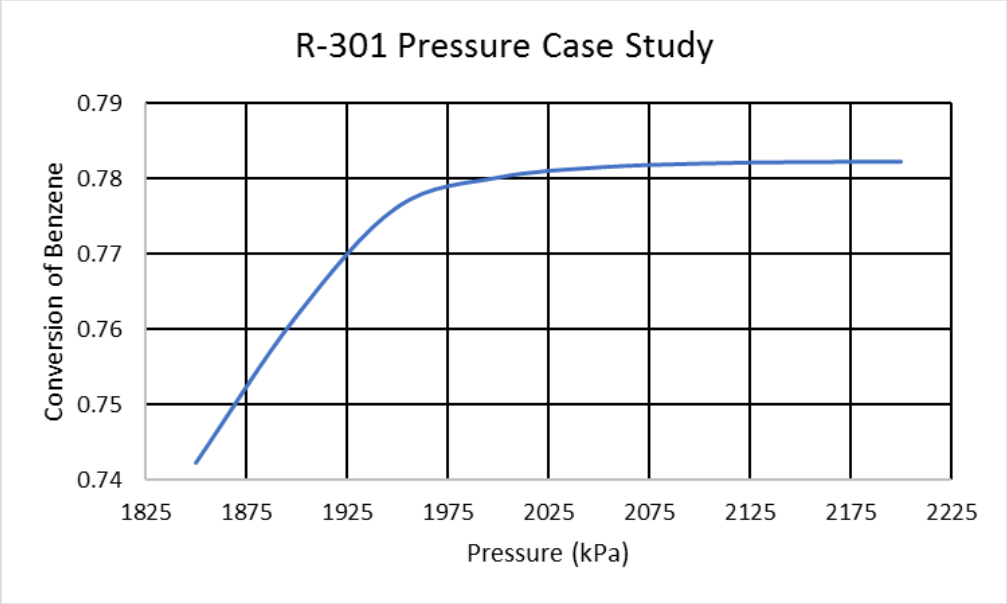
R-301 temperature optimization data and resultant NPV at each temperature. The ■ denotes the optimum temperature and, thus, the chosen point.



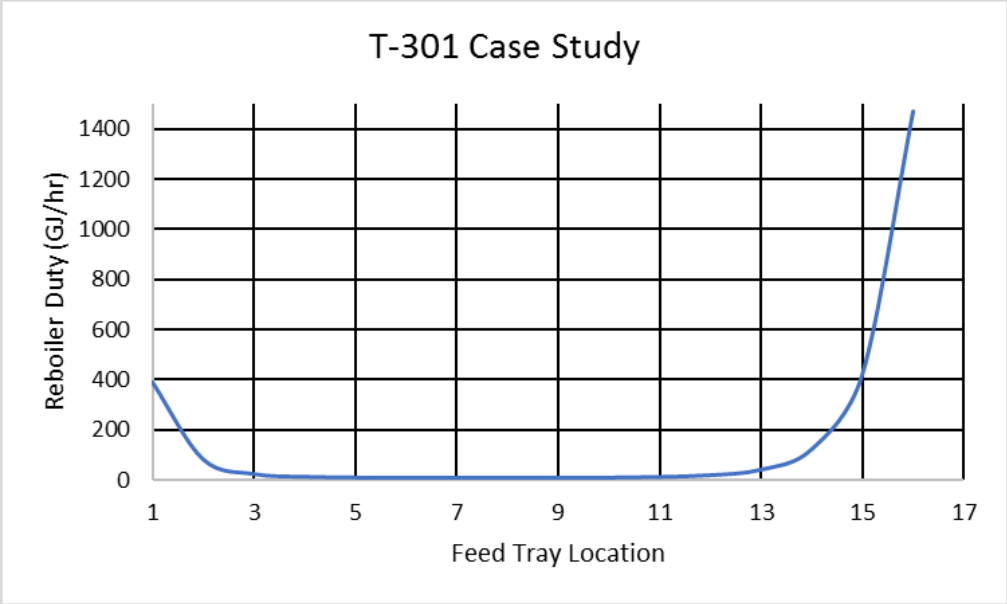
R-301 catalyst bed volume optimization data and resultant NPV at each volume. The ■ denotes the value of the optimum volume and, thus, the chosen volume.

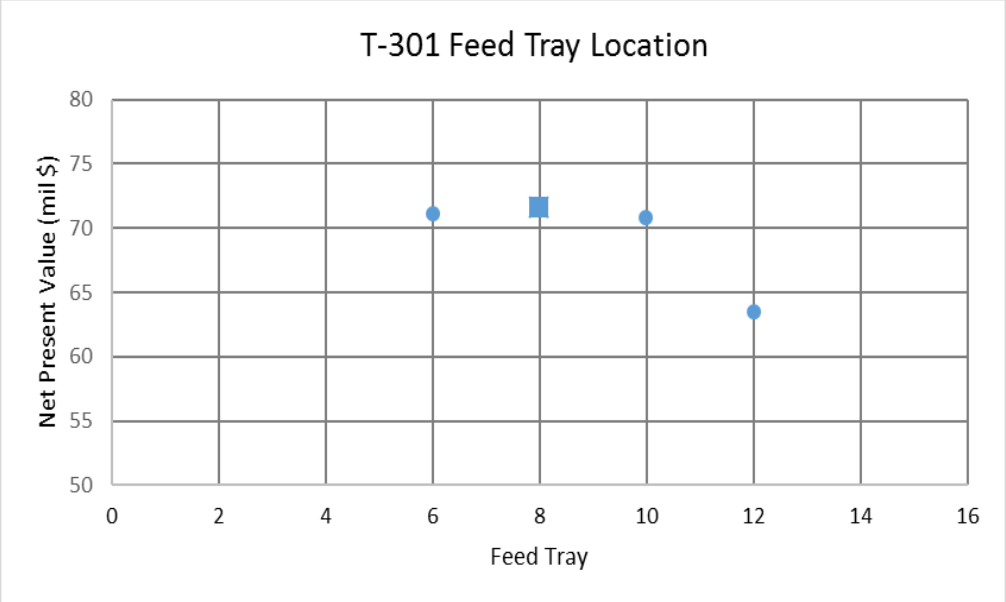
Appendix 7 (cont'd): Reactor Optimization and Pressure Case Study for Section II





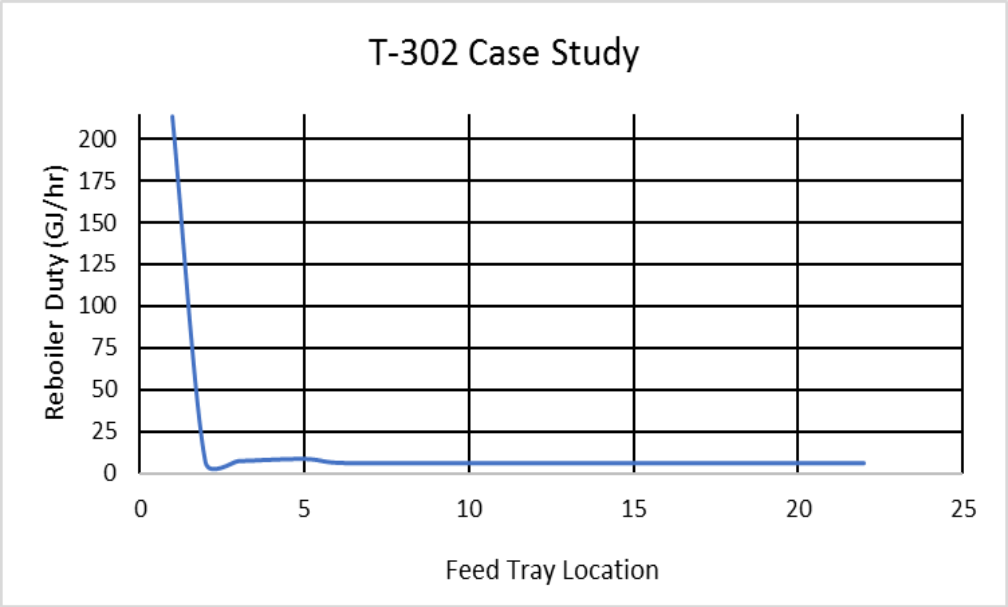
Appendix 8: T-301 Tray Location Case Study and NPV Optimization for Section II

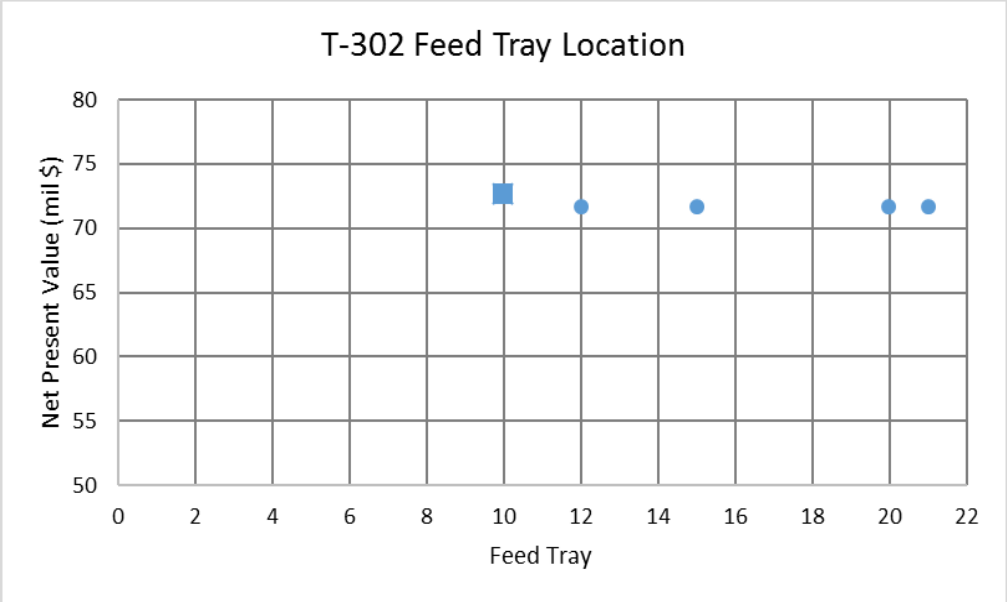




T-301 feed tray location optimization data and resultant NPV at each feed tray. The ■ denotes the optimum feed tray location.

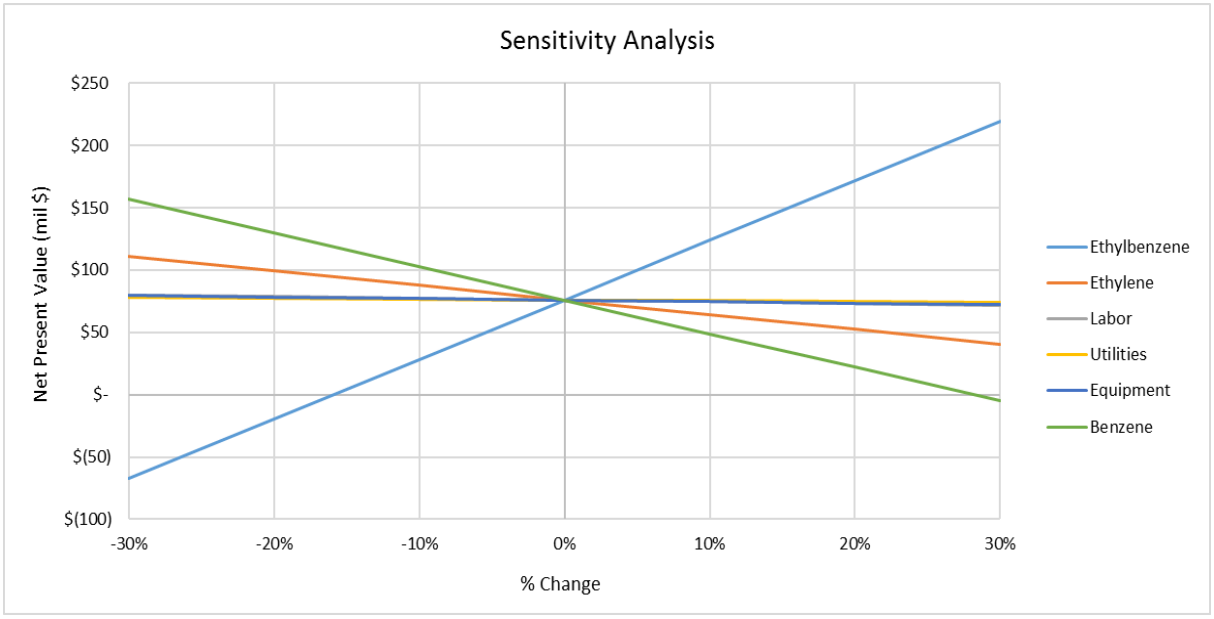
Appendix 9: T-302: Tray Location Case Study and NPV Optimization for Section II

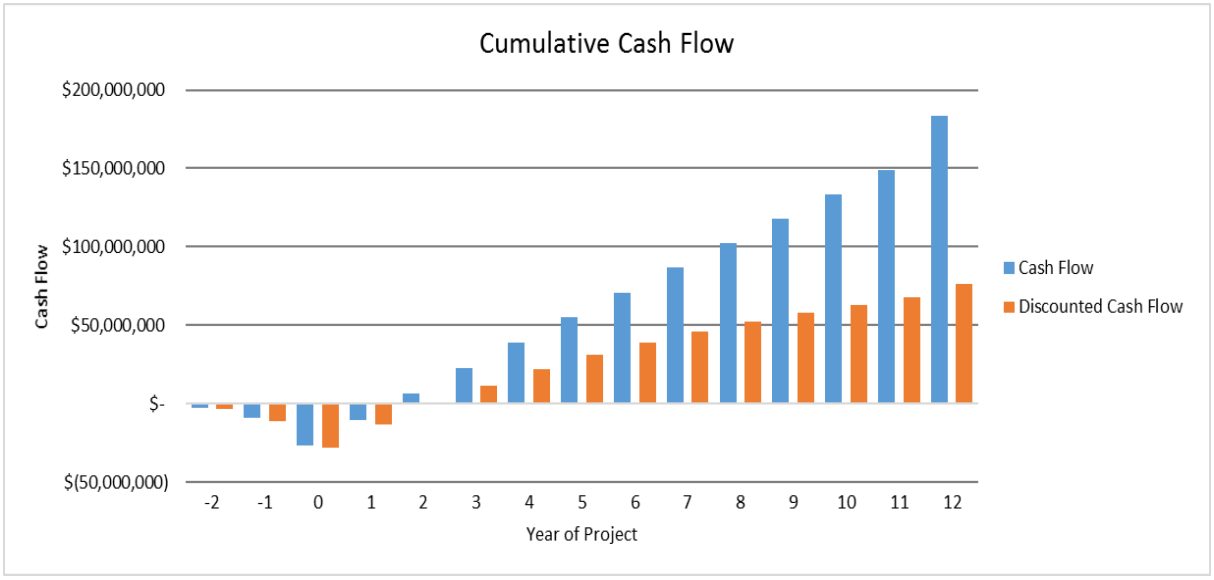




T-302 feed tray location optimization data and resultant NPV at each feed tray. The ■ denotes the optimum feed tray location.

Appendix 10: Sensitivity Analysis and Cash Flow Analysis for Section II





Appendix 11: Utility Costs for Section II

Utility Costs						
		Inlet				
Equipment	Desc	Mass (1000 kg/h)	Duty (GJ/h)	$/1000 kg	cost/h	cost/yr
E-301	bfw	0	-	$ 2.45	$0.00	$ -
E-302	bfw	0	-	$ 2.45	$0.00	$ -
E-303	bfw	0	-	$ 2.45	$0.00	$ -
E-304	bfw	3.92	-	$ 2.45	$9.61	$ 79,954.99
			Duty (GJ/h)	$/GJ	cost/h	cost/yr
E-306	lps (120 kPa)	4.12	9.24	$ 14.05	$ 129.82	$ 1,080,343.61
E-308	hps (140 kPa)	2.45	5.47	$ 17.70	$ 96.85	$ 805,963.40
		Volume (m3/h)		$/1000 m3 or $/GJ		
E-305	cw	112.02	-	$ 14.80	$ 1.66	$ 13,797.24
E-307	cw	-	8.30	$ 0.35	$ 2.94	$ 24,438.44
E-309	cw	-	5.54	$ 0.35	$ 1.96	$ 16,321.95
H-301	-	-	5.61	11.1	$ 62.27	$ 518,237.74
			Duty (kW)	$/kWh	$/h	cost/yr
D-301 A/B	-	-	16.65	$ 0.06	$ 1.00	$ 8,315.12
D-302 A/B	-	-	1.11	$ 0.06	$ 0.07	$ 554.80
D-303 A/B	-	-	1.11	$ 0.06	$ 0.07	$ 554.80

Utility Costs							
		Outlet					NET
Equipment	Desc	Desc	$/kg	$/h	cost/yr		cost/yr
E-301	hps	hps	$ 29.97	$ -	$ -		$ -
E-302	hps	hps	$ 29.97	$ -	$ -		$ -
E-303	hps	hps	$ 29.97	$ -	$ -		$ -
E-304	lps	lps	$ 29.29	$ 114.86	$ 955,870.06		$ 875,915.07
			Duty (GJ/h)	$/GJ	cost/yr		
E-306	bfw	bfw	$ 2.45	$ 10.09	$ 83,948.58		$ (996,395.03)
E-308	bfw	bfw	$ 2.45	$ 6.01	$ 49,985.17		$ (755,978.23)
		Volume (m3/h)		$/1000 m3 or $/GJ			
E-305	-	-	-	-	-		$ (13,797.24)
E-307	-	-	-	-	-		$ (24,438.44)
E-309	-	-	-	-	-		$ (16,321.95)
H-301	-	-	-	-	-		$ (518,237.74)
			Duty (kW)	$/kWh	$/h		
D-301 A/B	-	-	-	-	-		$ (8,315.12)
D-302 A/B	-	-	-	-	-		$ (554.80)
D-303 A/B	-	-	-	-	-		$ (554.80)
					Total Cost/yr=	$ (1,314,193.46)	utilities

Appendix 12: Cost of Manufacturing for Section II

Cost of Labor						
P	0					
N_{NP}	11					
$N_{OL\ (unrounded)}$	2.97					
Weeks per year	49	weeks per year				
Shifts per week	245	shifts per year				
Shifts/year	1095	shifts per year				
Shifts/op	4.5000	shifts per operator				
# Employees	13.36	employees needed		3%		
# Employees	14	employees hired	2021	2022	2023	2024
Labor Wages/per operator	$ 77,800.00	$/year2020	$ 80,134.00	$ 82,538.02	$ 85,014.16	$ 87,564.59
Total Employ Wages	$ 1,089,200.00	$/year	$ 1,121,876.00	$ 1,155,532.28	$ 1,190,198.25	$ 1,225,904.20

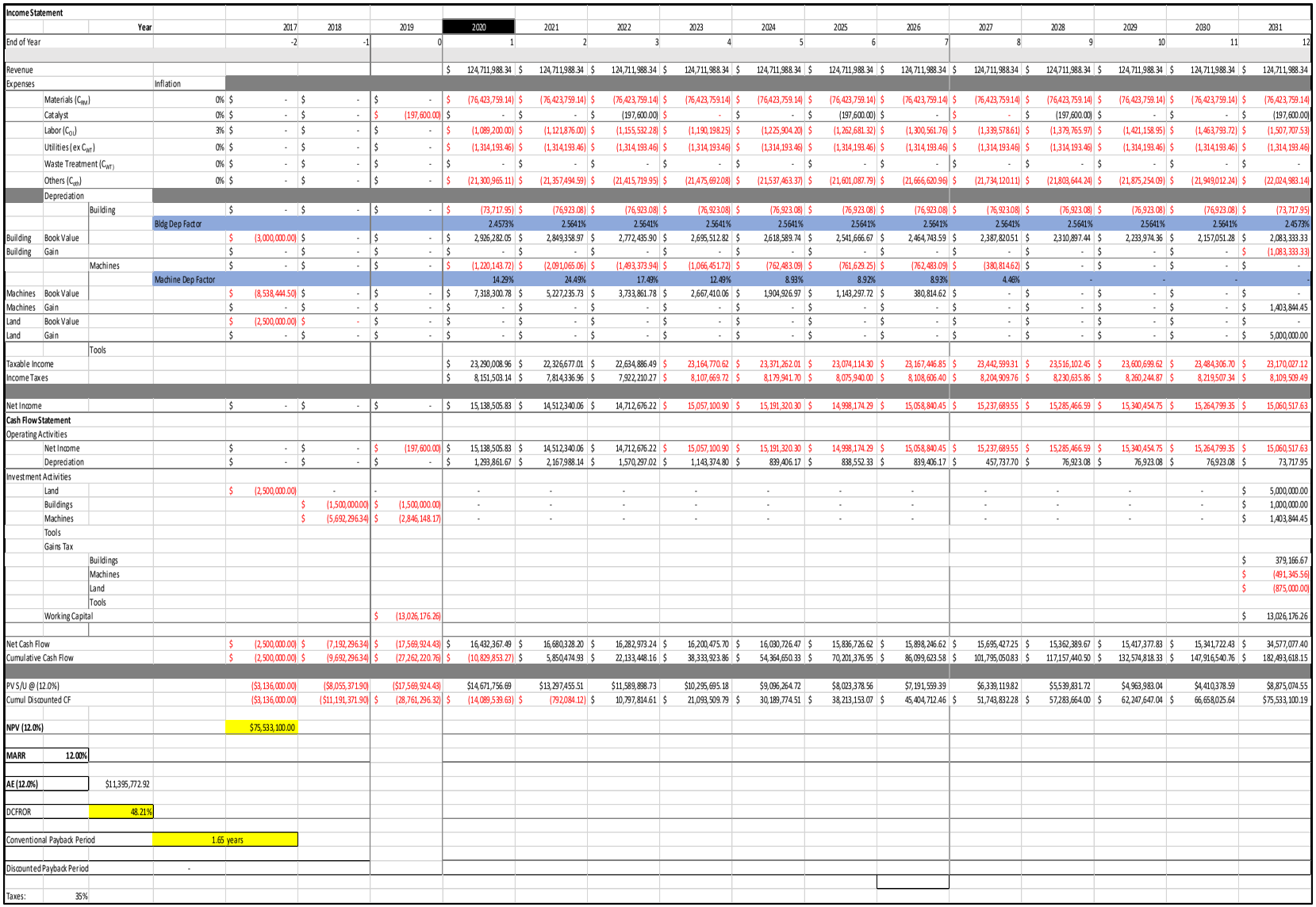
Sales					
	Price ($/tonne)	Flow (tonne/yr)	Cost ($/kg)	Cost ($/yr)	
Ethylbenzene	$ 1,485.00	80000.6161	1.485	$ 118,800,914.91	
	Price ($/GJ)	V* Flow (m^3/hr)	LHV (GJ/m^3)	Cost ($/yr)	
Fuel Gas (Flash Drum)	$ 11.10	614.73	0.10	$ 5,910,314.87	
Fuel Gas (Bottoms T302)	$ 11.10	0.04	0.20	$ 758.56	
Total Sales	$124,711,988.34	$/year			

Raw Materials				
Feed	Cost $/kg	Flow kg/hr	Cost $/yr	
Ethylene	$ 0.98	2859.09	$ 23,269,904.74	
Benzene	$ 0.85	7514.29	$ 53,153,854.39	
Total Raw Material Cost	$76,423,759.14	$/year		

Catalyst		
Cost	8	$/kg
Lifetime	3	years
Density	1,300	kg/m^3
Void Fraction	0.5	
Max Op T (°C)	525	°C
Cat- 301 (m^3)	19.00	
Cat- 301 (kg)	24700.00	
Total Volume	19.00	m^3
Total Weight	24700.00	kg
Cost per year	$ 197,600.00	$/year

Equipment Type	Number	N_{NP}
Particulate Handling	0	0
Compressors	0	0
Exchangers (vaporizers)	7	7
Heaters/Furnaces	1	1
Pumps*	6	0
Reactors	1	1
Towers	2	2
Vessels*	4	0
Total	21	11

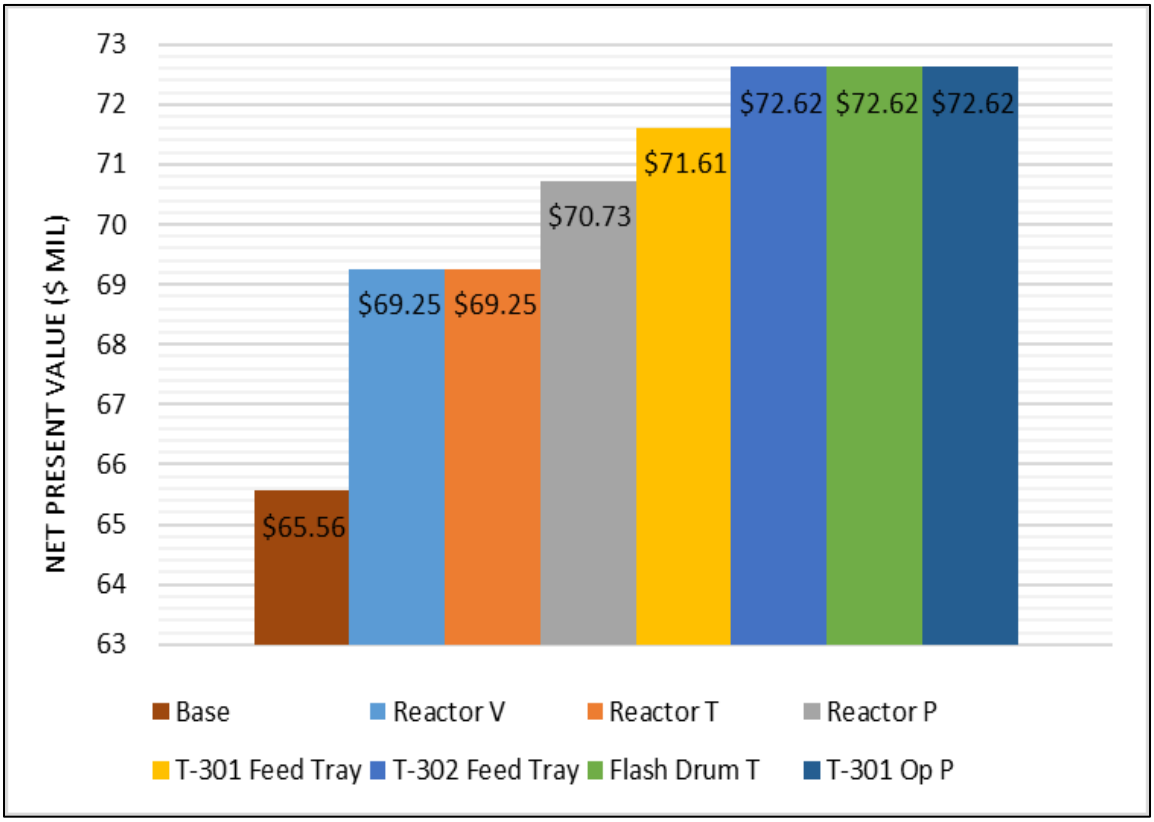
Operating Time:	
1	year
365	days/yr
8760	hrs/yr
0.95	Stream Factor
8322	hrs/yr operating



Income Statement																							
	Year			2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031					
End of Year				-2	-1	0	1	2	3	4	5	6	7	8	9	10	11	12					
Revenue							$ 124,711,988.34	$ 124,711,988.34	$ 124,711,988.34	$ 124,711,988.34	$ 124,711,988.34	$ 124,711,988.34	$ 124,711,988.34	$ 124,711,988.34	$ 124,711,988.34	$ 124,711,988.34	$ 124,711,988.34	$ 124,711,988.34					
Expenses			Inflation																				
	Materials (C_{RM})		0%	$ -	$ -	$ -	$ (76,423,759.14)	$ (76,423,759.14)	$ (76,423,759.14)	$ (76,423,759.14)	$ (76,423,759.14)	$ (76,423,759.14)	$ (76,423,759.14)	$ (76,423,759.14)	$ (76,423,759.14)	$ (76,423,759.14)	$ (76,423,759.14)	$ (76,423,759.14)					
	Catalyst		0%	$ -	$ -	$ (197,600.00)	$ -	$ -	$ (197,600.00)	$ -	$ -	$ -	$ (197,600.00)	$ -	$ -	$ (197,600.00)	$ -	$ (197,600.00)					
	Labor (C_{OL})		3%	$ -	$ -	$ -	$ (1,089,200.00)	$ (1,121,876.00)	$ (1,155,532.28)	$ (1,190,198.25)	$ (1,225,904.20)	$ (1,262,681.32)	$ (1,300,561.76)	$ (1,339,578.61)	$ (1,379,765.97)	$ (1,421,158.95)	$ (1,463,793.72)	$ (1,507,707.53)					
	Utilities (ex C_{WT})		0%	$ -	$ -	$ -	$ (1,314,193.46)	$ (1,314,193.46)	$ (1,314,193.46)	$ (1,314,193.46)	$ (1,314,193.46)	$ (1,314,193.46)	$ (1,314,193.46)	$ (1,314,193.46)	$ (1,314,193.46)	$ (1,314,193.46)	$ (1,314,193.46)	$ (1,314,193.46)					
	Waste Treatment (C_{WT})		0%	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -					
	Others (C_{oth})		0%	$ -	$ -	$ -	$ (21,300,965.11)	$ (21,357,494.59)	$ (21,415,719.95)	$ (21,475,692.08)	$ (21,537,463.37)	$ (21,601,087.79)	$ (21,666,620.96)	$ (21,734,120.11)	$ (21,803,644.24)	$ (21,875,254.09)	$ (21,949,012.24)	$ (22,024,983.14)					
	Depreciation																						
		Building					$ (73,717.95)	$ (76,923.08)	$ (76,923.08)	$ (76,923.08)	$ (76,923.08)	$ (76,923.08)	$ (76,923.08)	$ (76,923.08)	$ (76,923.08)	$ (76,923.08)	$ (76,923.08)	$ (73,717.95)					
		Bldg Dep Factor					2.4573%	2.5641%	2.5641%	2.5641%	2.5641%	2.5641%	2.5641%	2.5641%	2.5641%	2.5641%	2.5641%	2.4573%					
Building	Book Value			$ (3,000,000.00)	$ -	$ -	$ 2,926,282.05	$ 2,849,358.97	$ 2,772,435.90	$ 2,695,512.82	$ 2,618,589.74	$ 2,541,666.67	$ 2,464,743.59	$ 2,387,820.51	$ 2,310,897.44	$ 2,233,974.36	$ 2,157,051.28	$ 2,083,333.33					
Building	Gain			$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ (1,083,333.33)					
		Machines		$ -	$ -	$ -	$ (1,220,143.72)	$ (2,091,065.06)	$ (1,493,373.94)	$ (1,066,451.72)	$ (762,483.09)	$ (761,629.25)	$ (762,483.09)	$ (380,814.62)	$ -	$ -	$ -	$ -					
		Machine Dep Factor					14.29%	24.49%	17.49%	12.49%	8.93%	8.92%	8.93%	4.46%	-	-	-	-					
Machines	Book Value			$ (8,538,444.50)	$ -	$ -	$ 7,318,300.78	$ 5,227,235.73	$ 3,733,861.78	$ 2,667,410.06	$ 1,904,926.97	$ 1,143,297.72	$ 380,814.62	$ -	$ -	$ -	$ -	$ -					
Machines	Gain			$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ 1,403,844.45					
Land	Book Value			$ (2,500,000.00)	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -					
Land	Gain			$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ 5,000,000.00					
		Tools																					
Taxable Income							$ 23,290,008.96	$ 22,326,677.01	$ 22,634,886.49	$ 23,164,770.62	$ 23,371,262.01	$ 23,074,114.30	$ 23,167,446.85	$ 23,442,599.31	$ 23,516,102.45	$ 23,600,699.62	$ 23,484,306.70	$ 23,170,027.12					
Income Taxes							$ 8,151,503.14	$ 7,814,336.96	$ 7,922,210.27	$ 8,107,669.72	$ 8,179,941.70	$ 8,075,940.00	$ 8,108,606.40	$ 8,204,909.76	$ 8,230,635.86	$ 8,260,244.87	$ 8,219,507.34	$ 8,109,509.49					
Net Income				$ -	$ -	$ -	$ 15,138,505.83	$ 14,512,340.06	$ 14,712,676.22	$ 15,057,100.90	$ 15,191,320.30	$ 14,998,174.29	$ 15,058,840.45	$ 15,237,689.55	$ 15,285,466.59	$ 15,340,454.75	$ 15,264,799.35	$ 15,060,517.63					
Cash Flow Statement																							
Operating Activities																							
	Net Income			$ -	$ -	$ (197,600.00)	$ 15,138,505.83	$ 14,512,340.06	$ 14,712,676.22	$ 15,057,100.90	$ 15,191,320.30	$ 14,998,174.29	$ 15,058,840.45	$ 15,237,689.55	$ 15,285,466.59	$ 15,340,454.75	$ 15,264,799.35	$ 15,060,517.63					
	Depreciation			$ -	$ -	$ -	$ 1,293,861.67	$ 2,167,988.14	$ 1,570,297.02	$ 1,143,374.80	$ 839,406.17	$ 838,552.33	$ 839,406.17	$ 457,737.70	$ 76,923.08	$ 76,923.08	$ 76,923.08	$ 73,717.95					
Investment Activities																							
	Land			$ (2,500,000.00)	-	-	-	-	-	-	-	-	-	-	-	-	-	$ 5,000,000.00					
	Buildings				$ (1,500,000.00)	$ (1,500,000.00)	-	-	-	-	-	-	-	-	-	-	-	$ 1,000,000.00					
	Machines				$ (5,692,296.34)	$ (2,846,148.17)	-	-	-	-	-	-	-	-	-	-	-	$ 1,403,844.45					
	Tools																						
	Gains Tax																						
		Buildings																$ 379,166.67					
		Machines																$ (491,345.56)					
		Land																$ (875,000.00)					
		Tools																					
	Working Capital					$ (13,026,176.26)												$ 13,026,176.26					
Net Cash Flow				$ (2,500,000.00)	$ (7,192,296.34)	$ (17,569,924.43)	$ 16,432,367.49	$ 16,680,328.20	$ 16,282,973.24	$ 16,200,475.70	$ 16,030,726.47	$ 15,836,726.62	$ 15,898,246.62	$ 15,695,427.25	$ 15,362,389.67	$ 15,417,377.83	$ 15,341,722.43	$ 34,577,077.40					
Cumulative Cash Flow				$ (2,500,000.00)	$ (9,692,296.34)	$ (27,262,220.76)	$ (10,829,853.27)	$ 5,850,474.93	$ 22,133,448.16	$ 38,333,923.86	$ 54,364,650.33	$ 70,201,376.95	$ 86,099,623.58	$ 101,795,050.83	$ 117,157,440.50	$ 132,574,818.33	$ 147,916,540.76	$ 182,493,618.15					
PV S/U @ (12.0%)				($3,136,000.00)	($8,055,371.90)	($17,569,924.43)	$14,671,756.69	$13,297,455.51	$11,589,888.73	$10,295,695.18	$9,096,264.72	$8,023,378.56	$7,191,559.39	$6,339,119.82	$5,539,831.72	$4,963,983.04	$4,410,378.59	$8,875,074.55					
Cumul Discounted CF				($3,136,000.00)	($11,191,371.90)	$ (28,761,296.32)	$ (14,089,539.63)	$ (792,084.12)	$ 10,797,814.61	$ 21,093,509.79	$ 30,189,774.51	$ 38,213,153.07	$ 45,404,712.46	$ 51,743,832.28	$ 57,283,664.00	$ 62,247,647.04	$ 66,658,025.64	$75,533,100.19					
NPV (12.0%)				$75,533,100.00																			
MARR	**12.00%**																						
AE (12.0%)		$11,395,772.92																					
DCFROR		48.21%																					
Conventional Payback Period			1.65 years																				
Discounted Payback Period			-																				
Taxes:	35%																						

Appendix 13: Income Statement for Section II

Appendix 14: NPV Change per Optimization for Section II



Appendix 15: Equipment Sizing Calculations for Section II

Pumps:

Each of the pumps used was positive displacement, and an efficiency of 75% was chosen based on the heuristics. The pumps used in the distillation tower condensers were assumed to be 1 kW. The theoretical power in the equation below is the power that is provided by a Pro/II equipment summary table.

$$P\ [kW] = \frac{Theoretical\ Power\ [kW]}{Efficiency}$$

P-301:

Pro/II power = 11.2407 kW

Efficiency = 75%

$$Total\ Power\ = \frac{11.2407\ kW}{0.75} = 15.0\ kW$$

Vessels:

Heuristics provide a hold-up time for each type of vessel, as well as specifying that each vessel should be half-full. They also say that the L/D should be within the range of 2.5 to 5, but 3 is the optimum. Vessels used in condensers for distillation towers should be sized using the reflux ratio of the given tower. For vessels that contain vapor, it is necessary to determine whether or not a demister is needed to force the liquid to the bottom of the vessel by using the velocities and seeing if the actual velocity is lower than the velocity without a demister.

$$V\ [m^3] = (Volumetric\ Flowrate\ [m^3/min]) \cdot (Holdup\ time\ [min])$$

$$D\ [m] = \sqrt[3]{\frac{4V}{3\pi}}$$

$$L\ [m] = 3D$$

$v\ [m/s] = k\sqrt{\frac{\rho(liq)}{\rho(vap)} - 1}$ k with demister = 0.11; k without demister = 0.0309

$$v\ actual\ [m/s] = \frac{Volumetric\ Flowrate\ [m^3/s]}{Cross\ sectional\ area\ [m^2]}$$

V-301:

Volumetric flowrate = 0.357 m3/min

Hold-up time = 30 min

$V = (0.357\ m^3/min)(30\ min)(2) = 21.41\ m^3$

$D = \sqrt[3]{\frac{4(21.41\ m^3)}{3\pi}} = 2.1\ m$

$L = 3D = 6.3\ m$

Reactors:

The heuristics for reactors give that the L/D should ideally be between 3-5, but the optimum is around 5. For our purposes, we assumed that the volume used in Pro/II was the volume of the bed, or the volume of catalyst within the reactor. For sizing and pricing, 2 meters were added to the length of the reactor to account for vapor distribution. The pressure drop

per unit length was also solved for using the Ergun equation, and the pressure drop found here was used in Pro/II.

$$D\ [m] = \sqrt[3]{\frac{4V}{5\pi}}$$

$$L\ [m] = 5D$$

$$L\ actual\ [m]\ = L + 2$$

$$V\ actual\ [m^3] = \frac{\pi D^2}{4}(L\ actual)$$

$$\frac{\Delta P}{L} = \frac{150v\mu(1-\varepsilon)^2}{\varphi^2 Dp^2\varepsilon^3} + \frac{1.75\rho v^2(1-\varepsilon)}{\varphi Dp\varepsilon^3},$$

Where v is velocity in m/s, μ is fluid viscosity in kg/m*s, ε is bed porosity, φ is particle sphericity, Dp is particle diameter in m, ρ is liquid density in kg/m3, ΔP is pressure drop in Pa, and L is reactor length in m.

R-301:

$$D = \sqrt[3]{\frac{4(19\ m^3)}{5\pi}} = 1.7\ m$$

$$L = 5(1.7\ m) = 8.5\ m$$

$$L\ actual\ = 8.5\ m + 2m = 10.5\ m$$

$$Vactual = \frac{\pi(1.7\ m)^2}{4}(10.5\ m) = 23.5\ m^2$$

$$\Delta P = 8.5(\frac{150(0.102)(1.72e{-}5)(1-0.5)^2}{1^2(0.001)^2(0.5)^3} + \frac{1.75(25.9)(0.102)^2(1-0.5)}{1(0.001)(0.5)^3})/1000 = 20.4\ kPa$$

Towers:

To size the towers, we generate a text report from Pro/II. From this text report, we find the tray with the highest volumetric flowrate of vapor and use that value and the corresponding density for the calculations below. The theoretical number of trays is given by the shortcut column used in Pro/II. The factor Fs is used to find the velocity, and the heuristics give that Fs should be within the range of 1.2-1.5 (m/s)(kg/m^3)0.5. We therefore used the midpoint of 1.35 for our calculations. Additionally, the heuristics say that the tray spacing in the tower should be 0.5 meters, 1.2 meters should be added to the top for vapor disengagement, and 1.8 meters should be added to the bottom for liquid level and reboiler return.

$$v\ [m/s] = \frac{1.35\ [(m/s)(kg/m^3)^{0.5}]}{(\rho(vap)\ [kg/m^3])^{0.5}}$$

$$D\ [m/s] = \sqrt{\frac{4(Volumetric\ flowrate\ [m^3/s])}{\pi(v\ [m/s])}}$$

$$Actual\ number\ of\ trays = \frac{Theoretical\ number\ of\ trays}{Efficiency}$$

$$H\ [m] = (Actual\ number\ of\ trays\ - 1)(0.5\ [m]) + 3[m]$$

$$V\ [m^3] = \frac{\pi(D\ [m])^2}{4}(H\ [m])$$

$$Tray\ area = \frac{\pi D^2}{4}$$

T-301:

$$v = \frac{1.35\ m/s(kg/m^3)^{0.5}}{(3.68\ kg/m^3)^{0.5}} = 0.7\ m/s$$

$$D = \sqrt{\frac{4(1.85\ m^3/s)}{\pi(0.7\ m/s)}} = 1.8\ m$$

$$Actual\ trays\ = \frac{16\ trays}{0.75} = 24\ trays$$

$$H = (24 - 1)(0.5\ m) + 3\ m = 14.5\ m$$

$$V = \frac{\pi(1.8\ m)^2}{4}(14.5\ m) = 38.1\ m^3$$

$$Tray\ area = \frac{\pi(1.8\ m)^2}{4} = 2.6\ m^2$$

Heat Exchangers:

To find the area of each heat exchanger, the three heat exchangers in series (E-303, E-304, and E-305) were simulated separately in Pro/II with utilities included. From this simulation, we were able to get the utility flow rates and heat exchanger zone duties over multiple zones. Based on the zone analysis that Pro/II gave us, we determined the heat transfer coefficients and temperature correction factors for each zone. The log mean temperature difference is calculated for each zone, and each of these numbers is used to find the area of each zone. Once each zone is calculated, we added these areas to find the total area of the heat exchanger. In the calculations given below, only the first two zones are shown to allow for a single area to be solved (since the first zone will not have a log mean temperature difference or an area). To find the areas of the condensers and reboilers

around the distillation towers, the duties and outlet stream temperatures are used, as well as the properties for each of the utilities, which were listed in the base case specifications. They are then calculated using the same equation as the other heat exchangers, shown below. To size the fired heater, we simply use the theoretical power, given in Pro/II, and the efficiency, which was used as 75% based on heuristics. Also from heuristics, a 20% safety factor is used to size the fired heater. Note in the calculations that units for temperature difference can be either celsius or kelvin, as they will be the same value.

$$Q\ [kW] = (U\ [W/m^2K])(A\ [m^2])(FT)(\Delta TLM\ [K])$$

$$U\ [W/m^2K] = (\frac{1}{hi\ [W/m^2K]} + \frac{1}{ho\ [W/m^2K]})^{-1},$$

where h_i and h_o are the heat transfer coefficients for each stream

$$\Delta TLM\ [K] = \frac{\Delta Th\ [K] - \Delta Tc\ [K]}{ln(\Delta Th\ [K]/\Delta Tc\ [K])},$$

where ΔT_h and ΔT_c are the hot and cold side temperature differences

$$P\ [kW] = \frac{Theoretical\ Power\ [kW]}{0.75} (1.2)$$

E-304:

Duty (10^6 kJ/hr)	Hot side temp (°C)	Cold side temp (°C)	h_i	h_o	U (W/m^2K)	F_T	TLM (K)	Area (m^2)
0	170	115	--	--	--	--	--	--
0.72	184.0	158.9	1000	5000	833.3	0.9	38.1	7.0

$$U = (\frac{1}{1000\ W/m^2K} + \frac{1}{5000\ W/m^2K} = 833.3\ W/m^2K$$

$$\Delta TLM = \frac{(184.0 - 158.9) - (170 - 115)}{ln((184.0 - 158.9)/(170 - 115))} = 38.1\ K$$

Based on the flowrate of the benzene feed, which was 90% benzene and 10% toluene, we found that there were 12.3 kmol/hr of toluene coming into the process. Since we assumed perfect separation (100% recovery), we assumed that we would have a tower that would have a stream leaving with all of this toluene. This stream is specified to only be 99.5 mol% pure, so we found that the total molar flowrate of this stream would be 12.4 kmol/hr. We converted all of this to kg and found that, based on the selling price of $0.91/kg, this amount would make $8.6 million. For comparison, we assumed that all of the toluene fed would instead be converted completely to EB then completely separated and sold. After converting the 99.8 mol% pure stream to kg, we found that the amount we would make from this EB would be approximately $16.1 million. The significant difference in these values made us decide that it would not be beneficial to try moving forward with this change.

Appendix 16: Base Case Process Description for Section II

Benzene and toluene are fed in Stream 1 on a 98 mol% basis of benzene. The two components are combined with the recycled benzene from Stream 21 in the storage tank, V-301. Benzene exits the storage drum in Stream 3 and is pumped, via P-301, up to a pressure of 2000 kPa and is fed through the convection zone of the fired heater, H-301 where the temperature is increased to 400°C.

Ethylene and ethane are fed to the plant in Stream 2 as 93 mol% ethylene. Stream 2 splits into three separate streams, Stream 4, Stream 5, and Stream 10. The stream leaving the H-301 is combined with Stream 4, to form Stream 6, which feeds the first reactor, R-301, on an 8:1 benzene to ethylene ratio. In the sequence of the reactors R-301, R-302, and R-303, the main reaction that occurs is the formation of EB:

$$C_2H_4 + C_6H_6 \rightarrow C_6H_5C_2H_5 \quad (1)$$

A side reaction between EB and ethylene to form DEB (DEB) also occurs:

$$C_6H_5C_2H_5 + C_2H_4 \rightarrow C_6H_4(C_2H_5)_2 \quad (2)$$

However, DEB reacts with benzene to further form EB:

$$C_6H_4(C_2H_5)_2 + C_6H_6 \rightarrow 2C_6H_5C_2H_5 \quad (3)$$

Additionally, the toluene from the feed reacts with ethylene to form EB and propylene:

$$C_6H_5CH_3 + 2C_2H_4 \rightarrow C_6H_5C_2H_5 + C_3H_6 \quad (4)$$

Stream 7 leaves R-301 to combine with Stream 5, and is sent through a heat exchanger, E-301, to decrease the temperature to 380°C. Stream 8, the effluent from E-301, is fed to R-302, for further conversion to EB, with the side reactions simultaneously occurring. The

effluent from R-302 is mixed with Stream 10 to be cooled to 380°C in E-302. The cooled stream, Stream 11, is fed to the final reactor of the sequence, R-303, in which the previously mentioned reactions occur, for maximum production of EB. After R-303, the exiting stream, Stream 12, is mixed with Stream 13 to form Stream 14. Stream 14 enters the series of heat exchangers E-303, E-304, and E-305 to lower the temperature of each effluent stream to 280°C, 170°C, and 80°C, respectively.

Before the stream from E-305 is fed to the Flash Drum, V-302, the pressure is decreased to 110 kPa through a valve. In V-302, a vapor-liquid separation occurs, where the vapor leaves the plant in Stream 15 as fuel gas. The liquid-phase stream, Stream 16, is then fed to the first tower, T-301. The unreacted benzene is separated as overhead in T-301 and exits at 110 kPa, to be condensed in E-307, then fed to the reflux drum and pump, V-303 and P-302, respectively. It is then split into Stream 17 and the reflux to be fed back into T-301. Stream 17 contains the unreacted benzene which will be further recycled. EB and additional impurities exit T-301 with part returning to the tower through the reboiler, E-306, and the remainder of the bottoms leaving as Stream 18 to be fed to T-302.

Separation of EB and DEB occurs in T-302. EB exits in the distillate, after being fed to the heat exchanger, E-309, the vessel, V-304, and the pump, P-303, in a similar condenser series as described in T-301. The distillate that is not returned to T-302 as reflux exits the plant in Stream 19 at 99.8 mol% EB as the final product. The effluent from the bottom of T-302 is either fed through the reboiler, E-308, to be returned to the tower or exits as the DEB recycle in Stream 20. Stream 20 is further fed to a pump, P-304, to increase the pressure to 2000 kPa. It is then mixed with Stream 22 to form Stream 23, which is fed to the radiant portion of the fired heater, H-301, and exits at a temperature of 500°C, before

being fed to R-304. Because the stream being fed to R-304 contains mostly benzene and DEB, only Reaction 3 occurs in R-304, which is the formation of EB. The effluent from R-304 is Stream 13, which, as previously mentioned, is mixed with Stream 12, to form the feed to R-301 as Stream 14.

Finally, the distillate from T-301, Stream 17, is recycled and split into two streams. The first split, is fed to the pump, P-305, and exits as Stream 22. The second stream from the split is Stream 21, which is fed to V-301 to be mixed with Stream 1.

Appendix 17: Optimized Case Process Description for Section II

Benzene and toluene are fed in Stream 1 on a 90 mol% basis of benzene. The two components are combined with the recycled benzene from Stream 17 in the storage tank, V-301. Benzene exits the storage drum in Stream 3 and is pumped, via P-301, to a pressure of 2000 kPa and is fed through the heat exchanger, E-310 before being fed into the fired heater, H-301 where the temperature is increased to 400°C.

Ethylene and ethane are fed to the plant in Stream 2 as 93 mol% ethylene. Stream 2 is mixed with the stream leaving H-301, stream 6, to form Stream 7. The mixed stream feeds the reactor, R-301, where the main reaction that occurs is the formation of EB:

$$C_2H_4 + C_6H_6 \rightarrow C_6H_5C_2H_5 \quad (1)$$

A side reaction between ethylbenzene and ethylene to form DEB (DEB) also occurs:

$$C_6H_5C_2H_5 + C_2H_4 \rightarrow C_6H_4(C_2H_5)_2 \quad (2)$$

However, DEB reacts with benzene to further form EB:

$$C_6H_4(C_2H_5)_2 + C_6H_6 \rightarrow 2C_6H_5C_2H_5 \quad (3)$$

Additionally, the toluene from the feed reacts with ethylene to form EB and propylene:

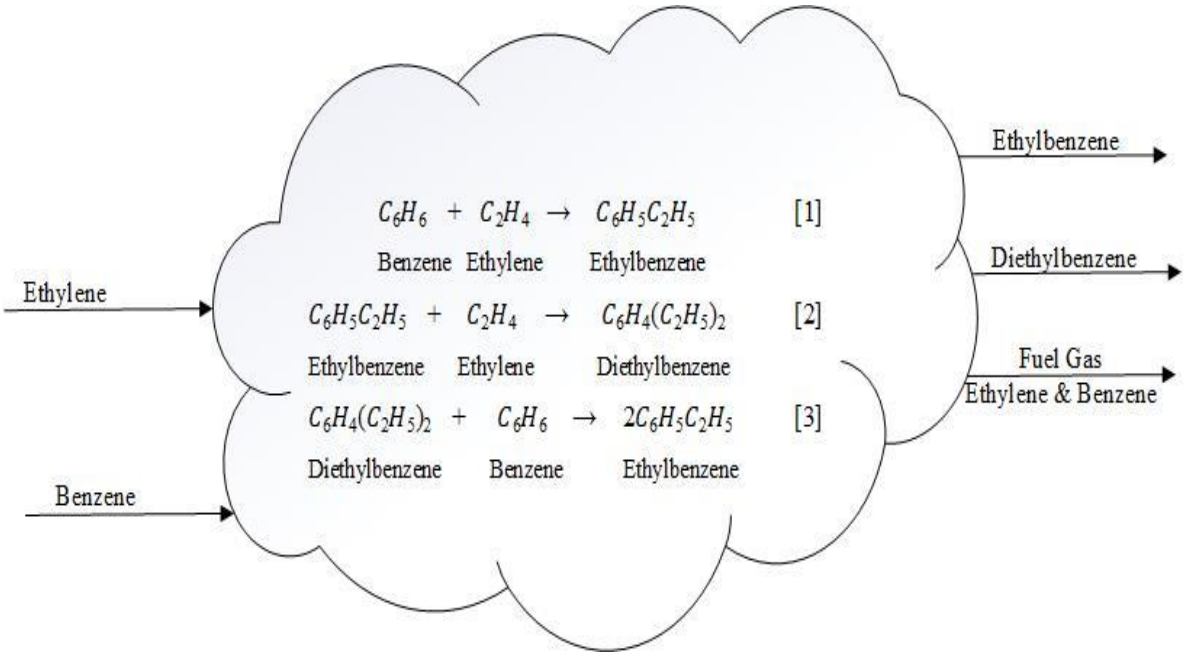
$$C_6H_5CH_3 + 2C_2H_4 \rightarrow C_6H_5C_2H_5 + C_3H_6 \quad (4)$$

Stream 7 leaves R-301 at a high temperature and is used as the hot process stream in E-310 to heat stream 4 lowering the effluent, stream 9, to 258°C. Stream 9 enters the series of heat exchangers, E-304, and E-305 to lower the temperature of each effluent stream to 170°C, and 80°C, respectively.

Before the stream from E-305, stream 11, is fed to the flash drum, V-302, the pressure is decreased to 110 kPa through a valve. In V-302, a vapor-liquid separation occurs, where the vapor leaves the plant in Stream 15 as fuel gas. The liquid-phase stream, Stream 16, is then fed to the first tower, T-301. The unreacted benzene is separated as overhead in T-301 and exits at 110 kPa, to be condensed in E-307, and then fed to the reflux drum and pump, V-303 and P-302, respectively. It is then split into Stream 17 and the reflux to be fed back into T-301. Stream 17 contains the unreacted benzene which will be further recycled. EB and additional impurities exit T-301 with part returning to the tower through the reboiler, E-306, and the remainder of the bottoms leaving as Stream 18 to be fed to T-302.

Separation of EB and DEB occurs in T-302. EB exits in the distillate, after being fed to the heat exchanger, E-309, the vessel, V-304, and the pump, P-303, in a similar condenser series as described in T-301. The distillate that is not returned to T-302 as reflux exits the plant in Stream 19 at 99.8 mol% EB as the final product. The effluent from the bottom of T-302 is either fed through the reboiler, E-308, and fed back into the tower, or exits as fuel gas. Finally, the distillate from T-301, Stream 17, is recycled and fed to V-301 to be mixed with Stream 1.

Appendix 18: Section III Process Concept Diagram for Liquid Phase EB Process



Appendix 19: Reactions and Reaction Kinetics for Section III

Reactions:

$$C_6H_6 + C_2H_4 \rightarrow C_6H_5C_2H_5 \quad [1]$$

Benzene Ethylene Ethylbenzene

$$C_6H_5C_2H_5 + C_2H_4 \rightarrow C_6H_4(C_2H_5)_2 \quad [2]$$

Ethylbenzene Ethylene Diethylbenzene

$$C_6H_4(C_2H_5)_2 + C_6H_6 \rightarrow 2C_6H_5C_2H_5 \quad [3]$$

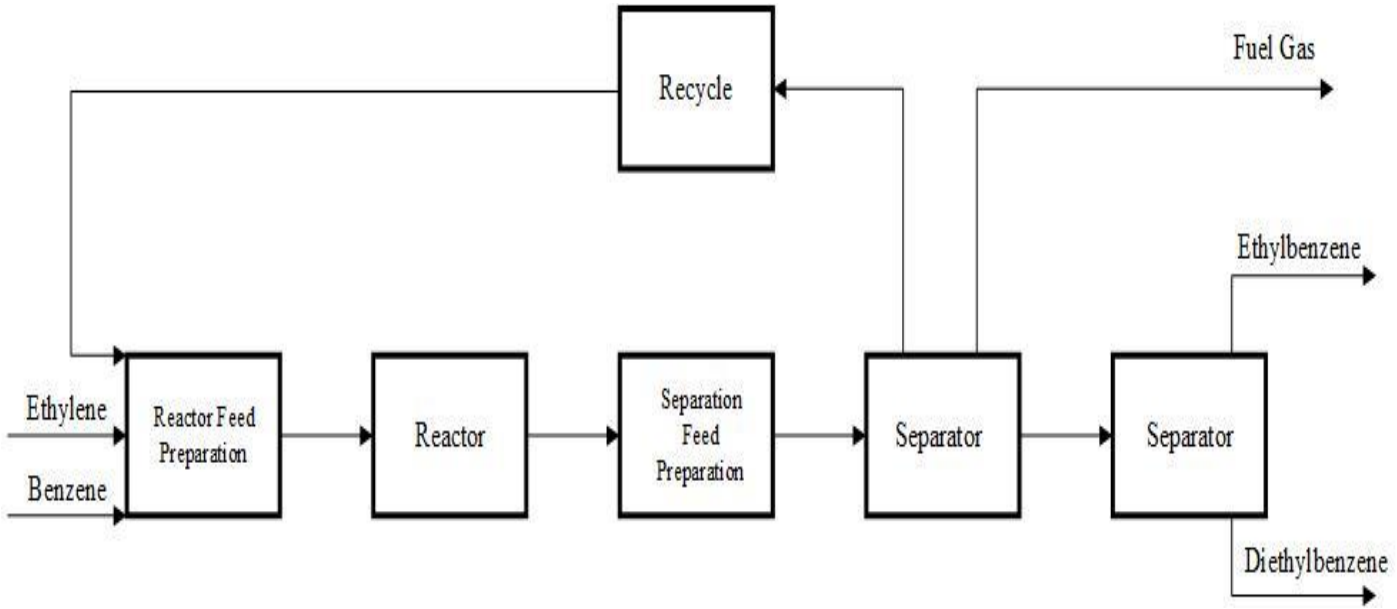
Diethylbenzene Benzene Ethylbenzene

Reaction Kinetics Rate Law:

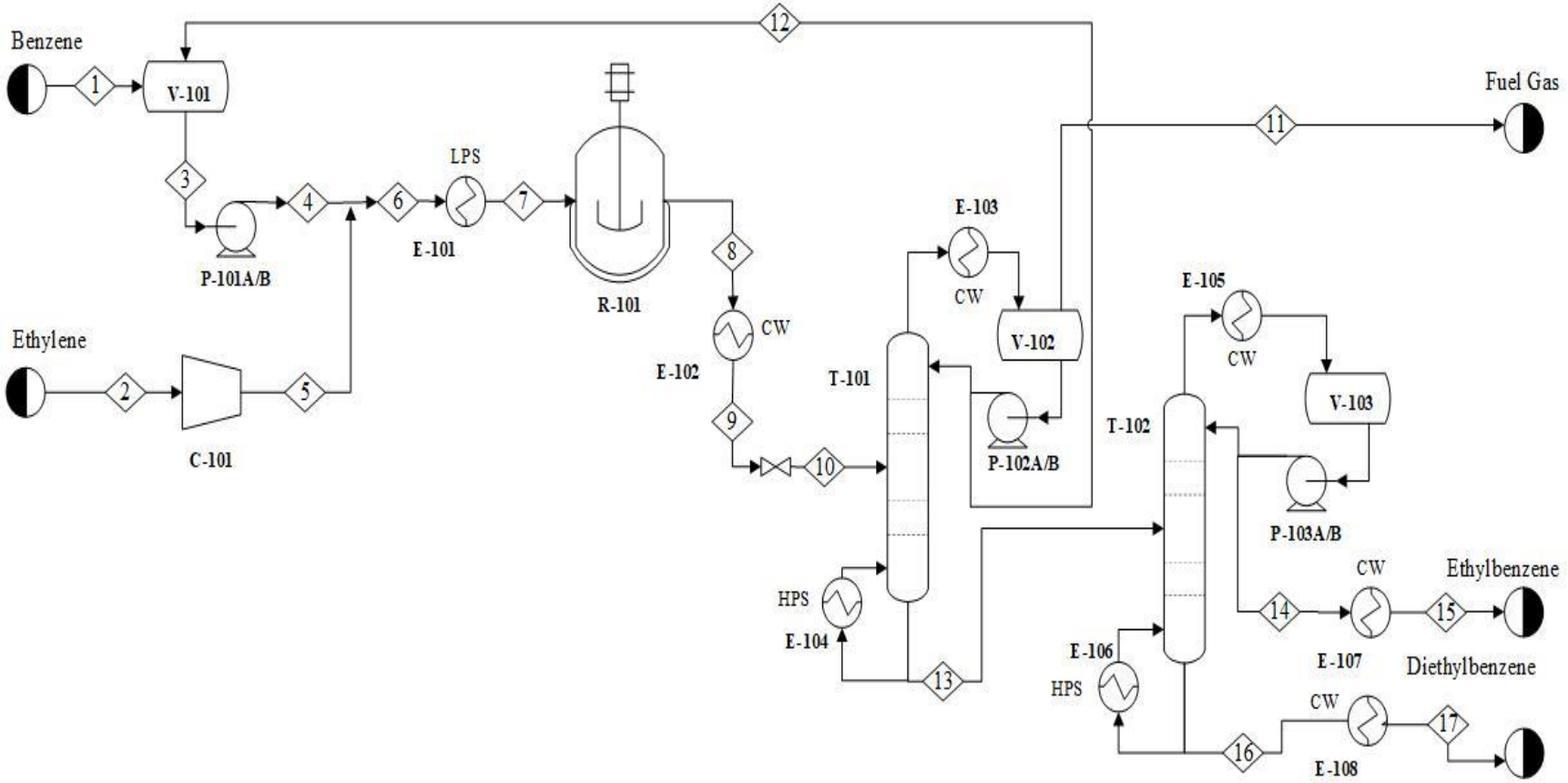
$$-r_i = k_{o,i}\, e^{-E_i/RT}\, C_{ethylene}^{a} C_{EB}^{b} C_{benzene}^{c} C_{DEB}^{d}$$

Reaction Kinetics:

i	E_i (kcal/kmol)	$k_{o,i}$	a	b	c	d
1	17,000	1.528×10^6	1	0	1	0
2	20,000	2.778×10^7	1	1	0	0
3	15,000	1,000	0	0	1	1



Appendix 20: Section III Block Flow Diagram



Appendix 21: Section III Process Flow Diagram

Appendix 22: Stream Flow Tables, Utility, and Equipment Summary for Section III

Table 22.1: Stream Tables

	1	**2**	**3**	**4**	**5**	**6**
Temperature (°C)	25.0	25.0	57.9	57.9	483.5	147.4
Pressure (atm)	1.0	1.0	1.0	54.8	54.8	54.8
Total (kmol/hr)	112.1	112.1	328.2	328.2	112.1	440.3
Total (kg/hr)	8759.7	3145.7	25624.8	25624.8	3145.7	28770.5
Molar Flowrates (kmol/hr)						
Ethylene		112.1	0.3	0.3	112.1	112.4
Benzene	112.1		327.8	327.8		327.8
Ethylbenzene			0.1	0.1		0.1
Diethylbenzene						

	7	**8**	**9**	**10**	**11**	**12**
Temperature (°C)	110.0	110.0	89.0	89.0	75.0	75.0
Pressure (atm)	54.6	54.6	54.4	2.0	1.0	1.0
Total (kmol/hr)	440.3	330.3	330.3	330.3	13.9	216.0
Total (kg/hr)	28770.5	28751.7	28751.7	28751.7	980.6	16865.1
Molar Flowrates (kmol/hr)						
Ethylene	112.4	2.3	2.3	2.3	2.1	0.3
Benzene	327.8	227.6	227.6	227.6	11.8	215.7
Ethylbenzene	0.1	90.5	90.5	90.5	0.0	0.1
Diethylbenzene		9.9	9.9	9.9		0.0

	13	**14**	**15**	**16**	**17**
Temperature (°C)	149.0	143.0	50.0	200.2	50.0
Pressure (atm)	1.3	1.2	1.0	1.5	1.3
Total (kmol/hr)	100.3	90.4	90.4	9.9	9.9
Total (kg/hr)	10906.0	9594.8	9594.8	1311.2	1311.2
Molar Flowrates (kmol/hr)					
Ethylene					
Benzene	0.1	0.1	0.1		
Ethylbenzene	90.4	90.3	90.3	0.1	0.1
Diethylbenzene	9.9	0.0	0.0	9.8	9.8

Appendix 22 (cont'd): Stream Flow Tables, Utility, and Equipment Summary for Section III

Table 22.2: Vessels Equipment Summary

V-101 9.7 m^3 Carbon Steel Maximum operating pressure = 2,200 kPa horizontal	**V-102** 9.4 m^3 Carbon Steel Maximum operating pressure = 2,200 kPa horizontal
V-103 6.1 m^3 Carbon Steel Maximum operating pressure = 2,200 kPa horizontal	

Table 22.3: Towers Equipment Summary

T-101 Carbon steel 60% efficient trays 0.5 m tray spacing maximum pressure rating of 300 kPa	**T-102** Carbon steel 60% efficient trays 0.5 m tray spacing maximum pressure rating of 300 kPa

Table 22.4: Pumps Equipment Summary

P-101 A/B Carbon steel- positive displacement Efficiency 75%	**P-102 A/B** Carbon steel- positive displacement Efficiency 75%
P-103 A/B Carbon steel- positive displacement Efficiency 75%	**C-101 A/B** Stainless steel-centrifugal Efficiency 75%

Table 22.5: Reactor Equipment Summary

R-101 carbon steel, CSTR V_{bed} = 150 m^3 maximum pressure rating of 2,200 kPa

Appendix 22 (cont'd): Stream Flow Tables, Utility, and Equipment Summary for Section III

Table 22.6: Heat Exchanger Equipment Summary

E-101 1-2 exchanger, fixed head, carbon steel process stream in tubes Q = 1950.1 MJ/h maximum pressure rating of 2,200 kPa	**E-102** 1-2 exchanger, fixed head, carbon steel process stream in tubes Q = 1058.0 MJ/h maximum pressure rating of 2,200 kPa
E-103 1-2 exchanger, fixed head, carbon steel process stream in tubes Q = 10850.1 MJ/h maximum pressure rating of 2,200 kPa	**E-104** 1-2 exchanger, kettle reboiler, carbon steel process stream in tubes Q = 32550.1 MJ/h maximum pressure rating of 2,200 kPa
E-105 1-2 exchanger, fixed head, carbon steel process stream in tubes Q = 6159.2 MJ/h maximum pressure rating of 2,200 kPa	**E-106** 1-2 exchanger, reboiler, carbon steel process stream in tubes Q = 18477.7 MJ/h maximum pressure rating of 2,200 kPa
E-107 1-2 exchanger, fixed head, carbon steel process stream in tubes Q = 1552.7 MJ/h maximum pressure rating of 2,200 kPa	**E-108** 1-2 exchanger, fixed head, carbon steel process stream in tubes Q = 237.6 MJ/h maximum pressure rating of 2,200 kPa

Appendix 22 (cont'd): Stream Flow Tables, Utility, and Equipment Summary for Section III

Table 22.7: Utility Summary

Stream Name	**lps to E-101**	**cw to E-102**	**cw to E-103**	**hps to E-104**
Temp (°C)	147.4	110.0	89.0	89.0
Pressure (kPa)	54.8	54.6	2.0	2.0
Flowrate (kmol/h)	440.3	330.3	216.0	216.0
Duty (MJ/h)	-1950.1	-1058.0	-10850.1	-32550.1
Stream Name	**cw to E-105**	**hps to E-106**	**cw to E-107**	**cw to E-108**
Temp (°C)	149.0	149.0	143.0	200.2
Pressure (kPa)	1.3	1.3	1.2	1.5
Flowrate (kmol/h)	100.3	100.3	90.4	9.9
Duty (MJ/h)	-6159.2	-18477.7	-1552.7	-237.6

Appendix 23: Section III – Reactor Feed Preparation Calculations (Streams 1 – 8)

Stream 1- Benzene Feed

Component flowrates (kmol/h):

	Formula	Value
Ethylene	0	0
Benzene	**Variable**	112.1
Ethylbenzene	0	0
Diethylbenzene	0	0
Total	Sum	112.1

Temperature: 25°C – Given
Pressure: 1 atm – Given

Stream 2- Ethylene Feed

Component flowrates (kmol/h):

	Formula	Value
Ethylene	**Variable**	112.1
Benzene	0	0
Ethylbenzene	0	0
Diethylbenzene	0	0
Total	Sum	112.1

Temperature: 25°C – Given
Pressure: 1 atm – Given

Stream 3- Mixing of Stream 1 and Stream 12 (Benzene Recycle)

Component flowrates (kmol/h):

	Formula	Value
Ethylene	= S1 + S12	0.3
Benzene	= S1 + S12	327.8
Ethylbenzene	= S1 + S12	0.1
Diethylbenzene	= S1 + S12	0
Total	= Sum	328.2

Temperature: 57.9°C - Calculated using the first law of thermodynamics and component heat capacities at constant pressure (Cp) as seen in Table 23.1

$$(T_3 - 25℃) \times (\Sigma \dot{n}_i Cp_i) = 0$$

Table 23.1

Heat Capacities of Liquids at 25°C	kJ/(kmol* K)
Ethylene	67.4
Benzene	135.7
Ethylbenzene	184.8
Diethylbenzene	257.9

Pressure: 1 atm

Stream 4: Effluent of P-101

Component flowrates (kmol/h):

	Formula	Value
Ethylene	= S3	0.3
Benzene	= S3	327.8
Ethylbenzene	= S3	0.1
Diethylbenzene	= S3	0
Total	= Sum	328.2

Temperature: 57.9°C – Same as Stream 3

Pressure: 54.8 atm – Pressure of R-101 + 0.2 to account for ΔP of 0.2 in E-101

$$P_{R-101} = -0.0005\frac{atm}{(°C)^2}T_{R-101}^2 + 0.4325\frac{atm}{(°C)}T_{R-101} + 13.056\ atm$$

$$P_{R-101} = 54.6\ atm$$

Stream 5: Effluent of C-101

Component flowrates (kmol/h):

	Formula	Value
Ethylene	= S2	112.1
Benzene	= S2	0
Ethylbenzene	= S2	0
Diethylbenzene	= S2	0
Total	= Sum	112.1

Temperature: 483.5°C – Calculated using the thermodynamic relation and k = 1.237:

$$T_5 = T_2 \times \left(\frac{P_5}{P_2}\right)^{\frac{(k-1)}{k}}$$

Pressure: 54.8 atm – Same as Stream 4

Stream 6: Mixing of Stream 4 and Stream 5

Component flowrates (kmol/h):

	Formula	Value
Ethylene	= S4 + S5	112.4
Benzene	= S4 + S5	327.8
Ethylbenzene	= S4 + S5	0.1
Diethylbenzene	= S4 + S5	0
Total	= Sum	440.3

Temperature: 147.4°C – Calculated using an enthalpy balance around the mixing points using component liquid heat capacities at constant pressure (Cp) for Stream 4 Table 23.1 and component heat capacities for gases and heat of vaporizations for Stream 5 as seen in Table 23.2 and Table 23.3.

$$Enthalpy_{out} - Enthalpy_{in} = 0$$

$$Enthalpy_{out} = (T_6 - 25℃) \times (\Sigma \dot{n}_i Cp_i)$$

$$Enthalpy_{in} = (T_4 - 25℃) \times (\Sigma \dot{n}_i Cp_i) + [\Sigma \dot{n}_i \times (A_{5,i} \times (T_5 - 25℃) + \frac{B_{5,i}}{2} \times (T_5 + 273.15)^2 - 298.15^2 + \frac{C_{5,i}}{3} \times (T_5 + 273.15)^3 - 298.15^3 + \frac{D_{5,i}}{4} \times (T_5 + 273.15)^4 - 298.15^4 + H_{vap,i})]$$

Table 23.2

Heat Capacities of Gases at 25°C	A	B	C	D
Ethylene	3.806E+00	1.566E-01	-8.348E-05	1.755E-08
Benzene	-3.392E+01	4.739E-01	-3.017E-04	7.130E-08
Ethylbenzene	-4.310E+01	7.072E-01	-4.811E-04	1.301E-07
Diethylbenzene	-3.742E+01	8.671E-01	-5.560E-04	1.411E-07

Table 23.3

Heat of Vaporization	kJ/kmol
Ethylene	14100
Benzene	33900
Ethylbenzene	41000
Diethylbenzene	45800

Pressure: 54.8 atm -Same as Streams 4 and 5

Stream 7: Effluent of E-101

Component flowrates (kmol/h):

	Formula	Value
Ethylene	= S6	112.4
Benzene	= S6	327.8
Ethylbenzene	= S6	0.1
Diethylbenzene	= S6	0
Total	= Sum	440.3

Temperature: 110°C – Set temperature for R-101

Pressure: 54.6 atm – Pressure of Stream 6 – 0.2 atm because of ΔP in E-101

Appendix 24: Section III – Reactor Calculations (Stream 8)

Stream 8: Effluent of R-101

Component flowrates (kmol/h): Calculated by performing a mole balance around R-101

$$Mole\ Balance: \quad In - Out + Generated = Accumulation$$

$$At\ Steady\ State: \quad In - Out + Generated = 0$$

Calculations for "In" (Stream 7): Calculated by first finding the volumetric flowrate ($\dot{V}_7$)

$$\dot{V}_7 = \Sigma \dot{n}_i V_{m,i} \quad [\frac{m^3}{h}]$$

	Stream 7 Concentrations ($\frac{kmol}{m^3}$)	
Component	Formula	Value
Ethylene	$= \frac{\dot{n_{7,E}}}{\dot{V_7}}$	3.73
Benzene	$= \frac{\dot{n_{7,B}}}{\dot{V_7}}$	10.88
Ethylbenzene	$= \frac{\dot{n_{7,EB}}}{\dot{V_7}}$	0.003
Diethylbenzene	$= \frac{\dot{n_{7,DEB}}}{\dot{V_7}}$	0.00

In:	Molar Flowrate (kmol/h)	
Component	Formula	Value
Ethylene	$= C_{E,7} \times \dot{V}_7$	112.4
Benzene	$= C_{B,7} \times \dot{V}_7$	327.8
Ethylbenzene	$= C_{EB,7} \times \dot{V}_7$	0.1
Diethylbenzene	$= C_{DEB,7} \times \dot{V}_7$	0

Calculations for "Out" (Stream 8): Same process as Stream 7, but concentrations are variables in Solver

	Stream 8 Concentrations ($\frac{kmol}{m^3}$)	
Component	Formula	Value
Ethylene	**Variable**	0.08
Benzene	**Variable**	7.55
Ethylbenzene	**Variable**	3.00
Diethylbenzene	**Variable**	0.33

Out:	Molar Flowrate (kmol/h)	
Component	Formula	Value
Ethylene	$= C_{E,8} \times \dot{V}_7$	2.3
Benzene	$= C_{B,8} \times \dot{V}_7$	227.6
Ethylbenzene	$= C_{EB,8} \times \dot{V}_7$	90.5
Diethylbenzene	$= C_{DEB} \times \dot{V}_7$	9.9

Calculations for "Generated": Calculated by first calculating the reaction rates (See Appendix 19 for Reaction kinetics)

General Equation: $$-r_i = k_{o,i}\, \mathrm{e}^{-E_i/RT}\, C_{ethylene}^{a} C_{EB}^{b} C_{benzene}^{c} C_{DEB}^{d}$$

Reaction Rates	Formula	Value (kmol/h/m^3)
r_1	$= -1.528 \times 10^6\, e^{-17{,}000/(1.987*101+273)} \times C_{E,8} \times C_{B,8} \times 3600$	-0.643
r_2	$= -2.778 \times 10^7\, e^{-20{,}000/(1.987*101+273)} \times C_{E,8} \times C_{EB,8} \times 3600$	-0.090
r_3	$= -1000\, e^{-15{,}000/(1.987*101+273)} \times C_{B,8} \times C_{DEB,8} \times 3600$	-0.025

Using a reactor volume of 150 m^3:

Generated:	Molar Flowrate (kmol/h)	
Component	Formula*	Value
Ethylene	$= (r_1 + r_2) \times V_{R-101}$	-110.08
Benzene	$= (r_1 + r_3) \times V_{R-101}$	-100.22
Ethylbenzene	$= (-r_1 + r_2 - 2r_3) \times V_{R-101}$	90.37
Diethylbenzene	$= (-r_2 + r_3) \times V_{R-101}$	9.85

*Formulas for the generated/consumed amount of each component were determined using the knowledge of reactor kinetics and the stoichiometry of the reactions.

Overall mole balance around R-101:

Component	**IN**	**-**	**OUT**	**+**	**GEN**	**=**	**ACC (0)**
Ethylene	112.4		2.3		-110.08		0
Benzene	327.8		227.6		-100.22		0
Ethylbenzene	0.1		90.5		90.37		0
Diethylbenzene	0		9.9		9.85		0

Conversion: $$\frac{Ethylene_{in} - Ethylene_{out}}{Ethylene_{in}} \times 100\% = 97.9\%$$

Component flowrates Cont. (kmol/h):

	Formula	Value
Ethylene	= "Out"	2.3
Benzene	= "Out"	227.6
Ethylbenzene	= "Out"	90.5
Diethylbenzene	= "Out"	9.9
Total	= Sum	330.3

Temperature: 110°C – Set temperature for R-101

Pressure: 54.6 atm – Pressure of R-101

$$P_{R-101} = -0.0005 \frac{atm}{(°C)^2} T_{R-101}^2 + 0.4325 \frac{atm}{(°C)} T_{R-101} + 13.056\ atm$$

$$P_{R-101} = 54.6\ atm$$

Appendix 25: Section III – Separation Feed Preparation Calculations

(Streams 9 – 10)

Stream 9: Effluent of E-102

Component flowrates (kmol/h):

	Formula	Value
Ethylene	= S8	2.3
Benzene	= S8	227.6
Ethylbenzene	= S8	90.5
Diethylbenzene	= S8	9.9
Total	= Sum	330.3

Temperature: 88.97°C – Calculated by performing a material balance on Stream 9

The vapor pressure of each component in Stream 10 was determined using Antoine's Equation:

$$P^*(T_{10}) = 10^{A_i - {B_i}/{(C_i + \boldsymbol{T_9}(K))}} \qquad [atm]$$

The amount of vapor and liquid of each component in stream 9 was found using Raoult's Law:

$$y_i P = x_i P^*$$

	Liquid mole fractions (x_i)		Vapor mole fractions (y_i)		K_i's from P*'s	
Component	Formula	Value	Formula	Value	Formula	Value
Ethylene	**Variable**	0.007	$= K_E \times x_E$	0.019	$= P_E / P_9$	2.707
Benzene	**Variable**	0.689	$= K_B \times x_B$	0.017	$= P_B / P_9$	0.024
Ethylbenzene	**Variable**	0.274	$= K_{EB} \times x_{EB}$	0.001	$= P_{EB} / P_9$	0.004
Diethylbenzene	$=1 - x_E - x_B - x_{EB}$	0.030	$= K_{DEB} \times x_{DEB}$	0.000	$= P_{DEB} / P_9$	0.001

Material Balance on Stream 9:

$$\dot{n}_{9,i} - \dot{n}_{9,liq,i} - \dot{n}_{9,vap,i} = 0$$

To provide enough constraints for Solver, an energy balance around the valve was performed: $$H_{10} - H_{9,liq} - H_{9,vap} = 0$$

Enthalpy of Stream 10:

$$H_{10} = (T_{10} - 25℃) \times \left(\Sigma \dot{n}_i Cp_i\right)$$

Enthalpy of Liquid Portion of Stream 9:

$$H_{9,liq} = (T_9 - 25℃) \times \left(\Sigma \dot{n}_i Cp_i\right)$$

Enthalpy of Vapor Portion of Stream 9:

$$H_{9,vap} = \Sigma \dot{n}_i \times (A_i \times (T_9 - 25℃) + \frac{B_i}{2} \times (T_9 + 273.15)^2 - 298.15^2 + \frac{C_i}{3} \times (T_9 + 273.15)^3 - 298.15^3 + \frac{D_i}{4} \times (T_9 + 273.15)^4 - 298.15^4 + H_{vap,i})$$

Pressure: 54.4 atm – Pressure of Stream 8 – 0.2 atm because of ΔP in E-102

Stream 10: Feed to T-101

Component flowrates (kmol/h):

	Formula	Value
Ethylene	= S9	2.3
Benzene	= S9	227.6
Ethylbenzene	= S9	90.5
Diethylbenzene	= S9	9.9
Total	= Sum	330.3

Temperature: 88.97°C – Calculated by determining the bubble point of Stream 10, using Antoine's Law and Raoult's Equation in a similar manner as done for Stream 9

Pressure: 2 atm – Chosen to aid in separation

Appendix 26: Separation Calculations (Streams 11 – 17)

T-101:

Streams 11: Fuel Gas

Component flowrates (kmol/h): Determined using Antoine's Law and Raoult's Equation

$$\dot{n}_i = y_i \dot{n}_{11}$$

Vapor fraction:

$$y_i = x_i \times \frac{P_{12}^*}{P_{12}}$$

	Formula	Value
Ethylene	$= y_E \dot{n}_{11}$	2.1
Benzene	$= y_B \dot{n}_{11}$	11.8
Ethylbenzene	$= y_{EB} \dot{n}_{11}$	0.0
Diethylbenzene	$= y_{DEB} \dot{n}_{11}$	0.0
Total	= Sum	13.9

Temperature: 75°C – For storage as a fuel gas

Pressure: 1 atm – Operating pressure of T-101

Stream 12: Benzene Recycle

Component flowrates (kmol/h): Determined using Antoine's Law and Raoult's Equation

$$\dot{n}_i = x_i \dot{n}_{12}$$

Liquid fraction (x_i) found using Solver:

Component	Formula	Value
Ethylene	**Variable**	0.0012
Benzene	**Variable**	0.9984
Ethylbenzene	$=1 - x_E - x_B$	0.0004
Diethylbenzene	0	0

Flowrates:

	Formula	Value
Ethylene	$= x_E \dot{n}_{12}$	0.3
Benzene	$= x_B \dot{n}_{12}$	215.7
Ethylbenzene	$= x_{EB} \dot{n}_{12}$	0.1
Diethylbenzene	$= x_{DEB} \dot{n}_{12}$	0.0
Total	= Sum	216.0

Temperature: 75°C – Same as Stream 11

Pressure: 1 atm – Same as Stream 11

Stream 13: Bottoms of T-101, Feed to T-102

Component flowrates (kmol/h): Calculated using the recovery specifications

Recovery of Benzene to the Distillate: 99.95%

Recovery of Ethylbenzene to the Bottoms: 99.90%

	Formula	Value
Ethylene	0	0
Benzene	$= S_{10} \times (1 - 0.9995)$	0.1
Ethylbenzene	$= S_{10} \times 0.999$	90.4
Diethylbenzene	= S10	9.9
Total	= Sum	100.3

Temperature: 149.0°C – Calculated by using Antoine's Law and Raoult's Equation

Pressure: 1.3 atm – Tower specifications

To provide enough constraints for Solver, an mole balance around the T-101 was performed:

$$S_{10} - S_{12} - S_{13} - S_{11} = 0$$

T-102:

Stream 14: Distillate from T-102

Component flowrates (kmol/h): Calculated using the recovery specifications

Recovery of Ethylbenzene to the Distillate: 99.90%

Recovery of Diethylbenzene to the Bottoms: 99.90%

	Formula	Value
Ethylene	0	0
Benzene	= S13	0.1
Ethylbenzene	$= S_{13} \times 0.999$	90.3
Diethylbenzene	$S_{13} \times (1 - 0.999)$	0
Total	= Sum	90.4

Temperature: 142.96°C – Calculated by using Antoine's Law and Raoult's Equation

Pressure: 1.2 atm – Tower specifications

Stream 15: Ethylbenzene Product Stream

Component flowrates (kmol/h):

	Formula	Value
Ethylene	= S14	0
Benzene	= S14	0.1
Ethylbenzene	= S14	90.3
Diethylbenzene	= S14	0
Total	= Sum	90.4

Temperature: 50°C – Product storage requirements

Pressure: 1 atm – Pressure of Stream 14 – 0.2 atm because of ΔP in E-107

Stream 16: Bottoms of T-102

Component flowrates (kmol/h): Calculated using the recovery specifications

Recovery of Ethylbenzene to the Distillate: 99.90%

Recovery of Diethylbenzene to the Bottoms: 99.90%

	Formula	Value
Ethylene	0	0
Benzene	0	0
Ethylbenzene	$= S_{13} \times (1 - 0.999)$	0.1
Diethylbenzene	$S_{13} \times 0.999$	9.8
Total	= Sum	9.9

Temperature: 200.22°C – Calculated by using Antoine's Law and Raoult's Equation

Pressure: 1.5 atm – Tower specifications

Stream 17: Diethylbenzene By-Product Stream

Component flowrates (kmol/h):

	Formula	Value
Ethylene	= S16	0
Benzene	= S16	0
Ethylbenzene	= S16	0.1
Diethylbenzene	= S16	9.8
Total	= Sum	9.9

Temperature: 50°C – Product storage requirements

Pressure: 1.3 atm – Pressure of Stream 14 – 0.2 atm because of ΔP in E-108

Appendix 27: Equations

First Law of Thermodynamics: $(T_i - 25℃) \times (\Sigma \dot{n}_i Cp_i) = 0$ [1]

Thermodynamic Relation: $T_i = T_{i+1} \times \left(\frac{P_{i+1}}{P_i}\right)^{\frac{(k-1)}{k}}$ [2]

Conversion: $\frac{Ethylene_{in} - Ethylene_{out}}{Ethylene_{in}} \times 100\%$ [3]

Antoine's Equation: $P^*(T_i) = 10^{A_i - {B_i}/{(C_i + T_i(K))}}$ [4]

Raoult's Law: $y_i P = x_i P^*$ [5]

Pressure$_{R\text{-}101}$: $P_{R-101} = -0.0005 \frac{atm}{(°C)^2} T_{R-101}^2 + 0.4325 \frac{atm}{(°C)} T_{R-101} + 13.056\ atm$ [6]

Appendix 28: References

[1] “CAMEO Chemicals.” CAMEO Chemicals, National Oceanic and Atmospheric Administration. Web. 12 November 2017.

[2] Fogler, H. Scott. *Essentials of Chemical Reaction Engineering*. Prentice Hall, 2011.

[3] Turton, Richard, et al. *Analysis, Synthesis, and Design of Chemical Processes*. 4th ed., Pearson Education, Inc., 2012.

[4] McCabe, Warren L., et al. *Unit Operations of Chemical Engineering*. 7th ed., McGraw-Hill, 2005.